

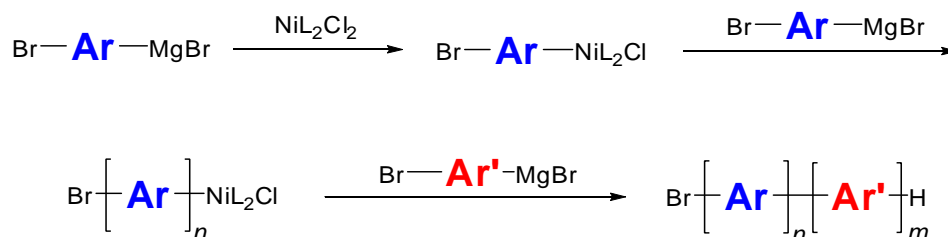
Synthesis of All-Conjugated Block Copolymers by Controlled Chain-Growth Condensation Polymerizations

Kathy Beckner Woody

School of Chemistry and Biochemistry, 901 Atlantic Drive, Atlanta, GA 30332-0400

kbeckner3@gatech.edu

ABSTRACT



Fully conjugated block copolymers can provide access to interesting new morphologies and electronic phenomena; however these materials have generally required complex syntheses. This review explores recent efforts to prepare all-conjugated block copolymers using chain-growth condensation polymerizations. This method provides simple routes to diblock copolymers, provides the ability to precisely control segment length and results in lower polydispersity indices, opening the door for facile synthesis of a multitude of diblock copolymers.

In the 1970's, Heeger, MacDiarmid and Shirakawa first realized the ability of polyacetylene to conduct electricity, spawning tremendous research efforts in the synthesis and development of new conjugated polymers, and resulting in the award of a Noble Prize in 2000.¹ The driving force for this research is the potential to use semiconducting conjugated materials in applications such as solar cells, sensors, field-effect transistors and displays. The breadth of potential applications of conjugated polymers creates a constant need for the optimization of existing polymers and design of new conjugated polymers with tunable properties.

The majority of research on conjugated polymers to-date has focused on homopolymers and alternating copolymers.² Much less studied are all-conjugated block copolymers, which can be attributed to the challenges in

synthesizing these types of materials. The few reports of fully conjugated block copolymers suggest that these materials present interesting opportunities to impart new properties as a result of phase separation of the two blocks with formation of morphologies which may be advantageous in new applications.³

Conjugated polymers are often prepared by condensation polymerizations of dihalides and an appropriately substituted difunctional monomers (functional groups = Sn(R)₃,⁴ ZnX,⁵ B(OR)₃,⁶ and phosphonates⁷). However, condensation polymerizations

(3) (a) Scherf, U.; Gutacker, A.; Koenen, N. *Acc. Chem. Res.* **2008**, *41*, 1086. (b) Liang, Y.; Wang, H.; Yuan, S.; Lee, Y.; Gan, L.; Yu, L. *J. Mater. Chem.* **2007**, *17*, 2183.

(4) Bao, Z.; Chan, W. K.; Yu, L. *J. Am. Chem. Soc.* **1995**, *117*, 12426.

(5) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233.

(6) Schluter, A. D. *J. Polym. Sci. Part A* **2001**, *39*, 1533.

(7) Suzuki, Y.; Hashimoto, K.; Tajima, K. *Macromolecules*, **2007**, *40*, 6521.

(1) Shirakawa, H. *Angew. Chem. Int. Ed.* **2001**, *40*, 2574.

(2) (a) *Handbook of Conducting Polymers*, 2 ed.; T. Skotheim, J. R., R. Elsenbamer, Ed. Marcel Dekker: New York, 1998. (b) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. *Chem. Rev.* **2009**, *109*, 897. (c) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.

typically proceed with step growth kinetics that lead to polydisperse materials with polydispersity indices (PDI) greater than 2.⁸ Such step growth processes do not lend themselves to formation of well-defined block copolymers. This essay highlights a new approach towards synthesizing all-conjugated block copolymers using innovative chain growth condensation polymerizations. The living nature of these polymerizations mean that the segment lengths can be controlled and the resulting polymers have narrow polydispersities. The ease and versatility of this new synthetic route provides access to a wide array of diblock copolymers which will have unique electronic properties.

Synthesis of Conjugated Diblock Copolymers by Step Growth Polymerizations. Early approaches to the synthesis conjugated diblock copolymers proceeded by coupling of the individual blocks.⁹ This requires the preparation of the individual polymers with appropriate functionality at the termini, which can then be coupled together in a subsequent reaction (Figure 1A).

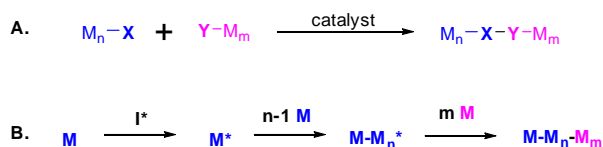


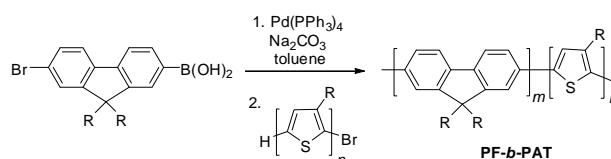
Figure 1. (A) Synthesis of diblock copolymers synthesized by step-growth polymerizations (B) Synthesis of diblock copolymers synthesized by chain-growth polymerizations.

There are several disadvantages associated with this synthetic approach. The end-groups of the final coupling reaction are present in very low concentrations leading to low yielding coupling of the polymer chains, which results in homopolymer impurities. The step growth polymerizations also give polymers with high PDIs, thus coupling the polydisperse polymer chains results in ill-defined materials such that it is difficult to tailor the lengths of the segments to attain control over copolymer assembly and properties

Another challenge associated with synthesizing each block using a step-growth polymerization is the inability to precisely control the end-groups of the polymers. Coupling two difunctional monomers can lead to polymers containing a mixture of the types functional group on each termini which could lead to tri-block copolymer and homopolymer impurities. Scherf addressed this issue by synthesizing a single monomer bearing each type of functional group, such that there would always be one type of each end group on every polymer chain. Poly(9,9-dialkylfluorene) was prepared by a Suzuki polymerization of the bromo-boronic acid

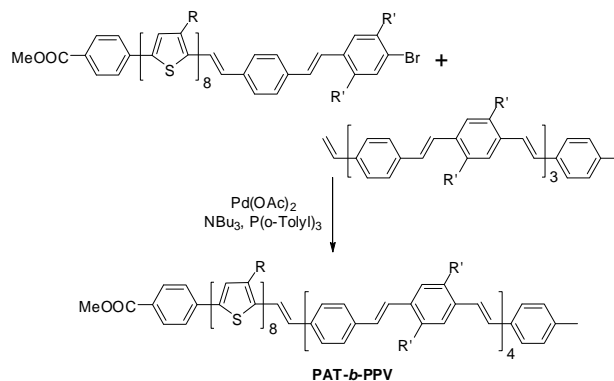
substituted monomer (Scheme 1).¹⁰ At the end of the polymerization, bromo-terminated poly(3-alkyl thiophene) was added to afford poly(9,9-dialkylfluorene)-block-poly(3-alkyl thiophene) (**PF-b-PAT**). While gel permeation chromatography (GPC) demonstrated that the desired block copolymers are formed, there are significant drawbacks to this synthetic method. Of particular concern was the inefficiency of the Suzuki coupling of the polymer chain ends, leading to the presence of homopolymer impurities; the resulting polymers had high PDIs even after extensive extraction. The lack of control over the molecular weight in step growth polycondensation reaction used to make the two individual blocks resulted in poorly defined materials.

Scheme 1. Synthesis of poly(9,9-dialkylfluorene)-block-poly(3-alkylthiophene).



In order to attain control of the segment lengths Yu and coworkers prepared a phenylene vinylene trimer bearing a terminal vinyl group and a thiophene octamer with a terminal bromo substituent, respectively. The end groups were subsequently coupled by a palladium-catalyzed Heck reaction (Scheme 2).¹¹ While this route has the advantage that the stepwise synthesis of the co-oligomers assures that the resulting polymers are monodisperse, this method requires many steps of synthesis and the molecular weights of the blocks are limited.

Scheme 2. Conjugated diblock copolymers synthesized by Heck coupling of oligo(phenylene vinylene) and oligothiophene.



(8) Flory, P. J. *Chem. Rev.* **1946**, *39*, 2656.

(9) Isomura, M.; Misumi, Y.; Masuda, T. *Polym. Bull.* **2001**, *46*, 291.

(10) Tu, G.; Li, H.; Forster, M.; Heiderhoff, R.; Balk, L. J.; Sigel, R.; Scherf, U. *Small* **2007**, *3*, 1001.

(11) Wang, H.; Ng, M.-K.; Wang, L.; Yu, L.; Lin, B.; Meron, M.; Xiao, Y. *Chem. Eur. J.* **2002**, *8*, 3246.

The dissimilar segments of the conjugated diblock materials described above undergo microphase separation to afford materials with interesting morphologies, such as cylindrical nanostructures,¹² and potential to tune fluorescence and bandgaps of the resulting polymers. However, challenges associated with the synthesis of well-defined materials has limited the impact of all-conjugated block copolymers thus far.³

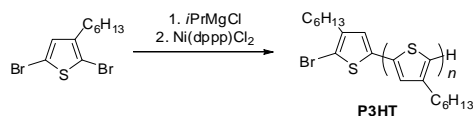
Given the lack of control over the polydispersity of polymers prepared by step growth condensation polymerizations, and the inefficiency of coupling polymer end groups, the recent development of chain-growth condensation polymerizations to prepare all-conjugated block copolymers present significant opportunities for the preparation of new materials with unique electronic properties.

Chain Growth Condensation Polymerizations. In contrast to the step growth kinetics of condensation polymerizations, addition polymerizations typically proceed by a chain growth process. In a chain growth polymerization, each polymer chain is grown from an initiator, and only reacts with subsequent monomer at the active termini. In the absence of pathways for termination or chain transfer this process leads to a “living” polymerization to afford well-defined polymers with narrow molecular weight distributions (PDI \approx 1) and control over the molecular weight. The addition of a second monomer to a living polymerization allows for further extension of the polymer chain to afford a block copolymer (Figure 1B).

The conversion of a condensation polymerization from a process involving step growth kinetics to one that proceeds by a chain growth process has only been reported recently. This requires the use of catalysts which selectively transfer reactivity to the terminus of the polymer chain upon addition of each monomer to the chain end.¹³

In 1995, McCullough¹⁴ developed the Grignard metathesis (GRIM) polymerization in which 2,5-dibromo-3-alkylthiophene was treated with a Grignard reagent followed by addition of a transition metal catalyst, producing regioregular poly(3-alkylthiophene) (Scheme 3).

Scheme 3. Synthesis of regioregular poly(3-alkylthiophene) by the GRIM polymerization.



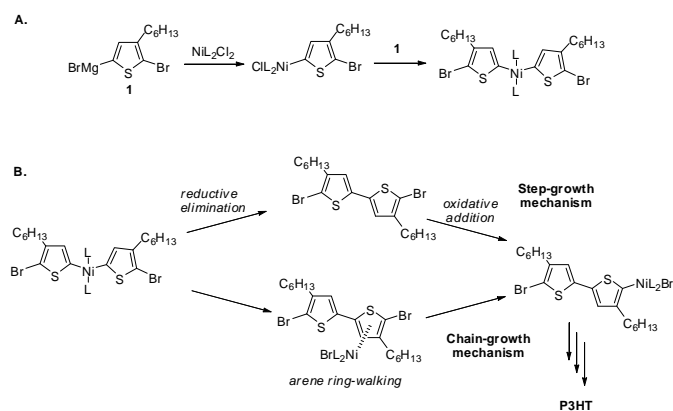
(12) (a) Güntner, R.; Asawapirom, U.; Forster, M.; Schmitt, C.; Stiller, B.; Tiersch, B.; Falcou, A.; Nothofer, H. -G. *Thin Solid Films* **2002**, *417*, 1-6. (b) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477.

(13) Yokoyama, A.; Yokozawa, T. *Macromolecules* **2007**, *40*, 4093.

(14) McCullough, R. D.; Williams, S. P.; Tristram-Nagle, S.; Jayaraman, M.; Ewbank, P. C.; Miller, L. *Synth. Metals* **1995**, *69*, 279.

The pathway for these polymerizations was originally formulated in terms of a nickel catalyzed coupling proceeding with step growth kinetics (Scheme 4B, top). However, evidence was soon collected to indicate that the polymerizations proceed with characteristics of a quasi-living process. Yokozawa and coworkers further modified this polymerization by synthesizing a 2-bromo-5-iodo-3-alkylthiophene which provided additional selectivity for the insertion of the metal, and demonstrated well-controlled polymerizations with narrow PDIs.¹⁵ Investigation of this reaction revealed that the polymerization takes place by a chain growth process, which they called a catalyst-transfer condensation polymerization (CTCP).

Scheme 4. (A) Addition of the nickel catalyst to the Grignard reagent (B) Top- original step-growth mechanism proposed by McCullough, Bottom- mechanism for the chain-growth catalyst transfer polymerization of 3-alkylthiophene.



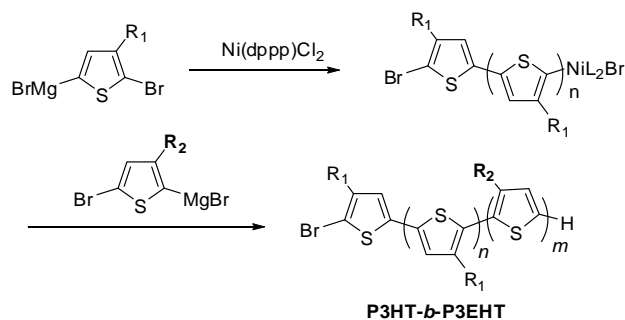
The polymerization proceeds by reaction of two equivalents of with nickel(II) to form a dithienylnickel(II) complex. The propagation step of the chain growth polymerization is a reductive elimination to form a thiophene-thiophene bond with *intramolecular transfer of the nickel to the chain end* by oxidative insertion into the thiophene-bromine bond. Thus, the reactive nickel center is transferred to the end of the growing polymer chain upon the addition of each monomer (Scheme 4B, bottom). The molecular weight of the polymerization is linearly proportional to the feed ratio of the monomer, consistent with a living polymerization. In addition, the molecular weight of the polymer can be precisely controlled by the amount of the Ni catalyst added.

Using this method it is possible to generate well-defined polymers with low PDIs, because this polymerization has living characteristics. Another important feature of a polymerization with living characteristics is the ability to prepare block copolymers by consecutive addition of a different monomer (Figure 1B).

(15) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169.

Synthesis of Conjugated Block Copolymers by the Chain Growth CTCP. An important attribute of living polymerizations is the ability to form block copolymers by the sequential addition of monomers. In 2008, Hashimoto and coworkers reported the first example of a one-pot synthesis of a fully conjugated diblock conjugated polymer by utilizing CTCP.¹⁶ In this study, 3-alkylthiophene monomers bearing hexyl and ethylhexyl side chains respectively were polymerized by sequential addition of the monomers (Scheme 5). The use of the catalyst transfer condensation polymerization to synthesize **P3HT-*b*-P3EHT** provided control over the segment lengths by varying the amounts of monomers added, and each block as a narrow polydispersity as a result of the chain-growth mechanism. Characterization of the resulting polymer, **P3HT-*b*-P3EHT**, revealed nanoscale segregation of the amorphous **P3EHT** blocks and the highly crystalline **P3HT** blocks. Varying the block lengths 50:50 75:25 produced different morphologies. Another advantage is the polymerization is carried out in one-pot reaction sequence, with no need to modify the individual blocks post polymerization, giving better yields with fewer impurities.

Scheme 5. Synthesis of poly(3-hexylthiophene)-*block*-poly(3-ethylhexylthiophene).



R_1 = hexyl, R_2 = ethylhexyl

Hashimoto's initial report was soon followed by publications from Ueda (a block copolythiophene consisting of crystalline poly(3-hexylthiophene and amorphous poly(3-phenoxyethylthiophene blocks),¹⁷ and Jenekhe (poly(3-butylthiophene)-*block*-poly(3-octylthiophene)).¹⁸ In the later case, even though both blocks are crystalline in nature the segments still undergo microphase separation to form nanostructured materials.

The synthetic method has also been applied to monomers other than thiophene (Figure 2). Yokozawa and coworkers used CTCP to polymerize a diblock copolymer of polythiophene and poly(*p*-phenylene),

P3HT-*b*-PPP.¹⁹ In this study they demonstrated that the order of addition of the monomers plays a critical role in the successful transfer of the catalyst from one block to the next. Initial polymerization of the more strongly π -donating thiophene monomer followed by addition of the *p*-phenylene monomer resulted in broad molecular weight distributions, suggesting that the transfer of the catalyst to the phenylene monomer was inefficient. Reversing the order of the polymerization led to a well-controlled polymerization with narrow polydispersities. The method was also extended to the controlled polymerization of *N*-substituted pyrroles and block copolymerization to afford poly(*N*-hexylpyrrole)-*block*-poly(*p*-phenylene).²⁰ With the wide selection of monomers available (including carbazole, fluorene²¹ and thieneopyrazine²²), there is potential for the synthesis of many different types of diblock copolymers using this method.

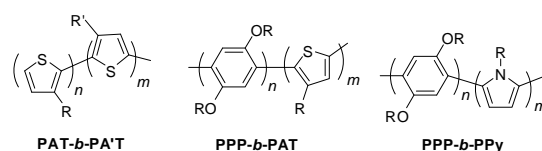


Figure 2. Examples of block copolymers that have been synthesized by the chain-growth CTCP.

Outlook. The development of chain growth CTCP provides a synthetic route which affords control over polymer structure, and affords access to novel all conjugated block copolymers. The polymerizations can be carried out in one pot, with good control over molecular weight and yielding polymers with narrow dispersities. The ability to control the segment length of the polymers offers opportunity to tune the morphologies and electronic properties of the block copolymers by varying the lengths of the individual blocks. As the versatility of the catalyst-transfer condensation polymerization expands a wide selection of monomers, polymer structures and architectures can be considered in the design of copolymers with new optoelectronic characteristics, varying electronic properties and potential to design polymers with telechelic endgroups from functional initiators.

(16) Zhang, Y.; Tajima, K.; Hirota, K.; Hashimoto, K. *J. Am. Chem. Soc.* **2008**, *130*, 7812.

(17) Ohshimizu, K.; Ueda, M. *Macromolecules* **2008**, *41*, 5289.

(18) Wu, P.-T.; Ren, G.; Li, C.; Mezzenga, R.; Jenekhe, S. *Macromolecules* **2009**, *42*, 2317.

(19) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *Chem. Lett.* **2008**, *37*, 1022.

(20) Yokoyama, A.; Kato, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2008**, *41*, 7271.

(21) Stefan, M. C.; Javier, A. E.; Osaka, I.; McCullough R. D. *Macromolecules* **2009**, *42*, 30.

(22) Wen, L.; Duck, B.; Dastoor, P. C.; Rasmussen, S. C. *Macromolecules* **2008**, *41*, 4576.