Synthesis of conjugated copolymers by combining different coupling reactions

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Despite the significant progress in the controlled synthesis of conjugated polymers using a Catalyst Transfer Condensative Polymerization, the possibilities regarding random and gradient copolymers remain very limited. Therefore, a novel concept is introduced, in which different organometallic functions are placed on the monomers in a copolymerization, meaning that different types of coupling reactions are combined. By using combinations of Grignard, organozinc, organoboron, organotin and organogold functional groups, the goal is to tune the reactivity ratio of the monomers. As such, it enables to tune the polymer structure without having to intervene during the polymerization, something which was impossible up to now. In this study, two randomly copolymerizing thiophene monomers are considered, whose reactivity is varied by altering the organometallic function. Despite the significant difference in reactivity between the chosen functional groups, it is found that most combinations nevertheless result in the formation of a random copolymer. However, the combination of the organotin and organogold monomer shows a gradient in the monomer consumption, with a preferential incorporation of the organogold monomer at low conversion. Although the copolymerization is not controlled, it is an indication that the use of different organometallic functions is a viable strategy to tune the gradient in a copolymerization.

Introduction

After the discovery of the controlled polymerization of poly(3-hexylthiophene) (P3HT) with Ni(dppp)Cl₂ (dppp = 1,3-bis(diphenylphosphino)propane) in 2004 by Yokozawa and McCullough, the synthesis of conjugated polymers evolved greatly.^{1,2} Apart from the large variety of monomers that can nowadays be polymerized in a controlled way thanks to the Catalyst Transfer Condensative Polymerization (CTCP), great progress has also been made in the formation of several types of copolymers and advanced architectures.^{3–5} As far as copolymers are concerned, the focus was mainly put on (multi) block copolymers, since the formation of random or gradient copolymers proved to be challenging. This is caused by the fact that the association of the catalyst to the polymer chain, the key prerequisite for obtaining a controlled CTCP, is highly dependent on the monomers that are incorporated. The preferential association of the catalyst to electron-rich monomers complicates the continued growth of the polymer after the incorporation of electron-poor monomer, because the catalyst is likely to remain associated to more electron-rich sequences. For block copolymers, this issue can be circumvented by polymerizing the more electron-poor monomer first, after which transition to electron-rich monomer

is easy.⁶ Of course, this strategy cannot be employed for random or gradient copolymers. As a consequence, only random copolymerizations of electronically very similar monomers have been achieved using CTCP, and gradient copolymers can only be obtained via syringe pump addition of one of both monomers that, again, needs to be very similar to the other to be able to copolymerize.^{7–12} Nevertheless, these gradient conjugated copolymers are of interest, because they show unique properties compared to homopolymers, block copolymers and random copolymers.^{13–15} On their own, they can give rise to otherwise inaccessible morphologies, but they can also serve as compatibilizer in blends of two homopolymers. Hence, a new and, to the best of our knowledge, unexplored strategy is considered in this study. Different organometallic functions are used on the two monomers in the same polymerization. It is clear that the organometallic function on the monomer greatly influences the reactivity of the monomer, meaning that the polymer structure can also be affected. A variety of different organometallic functions will be used to investigate the effect of combining different coupling reactions in the same copolymerization.

Results and Discussion

In first instance, only thiophene monomers are used, more specifically 3-hexyl- and 3-butylthiophene (Scheme 1). These are chosen because (1) the synthesis of poly(thiophene) using different organometallic functions and catalysts is widely investigated and (2) hexyl and butyl sidechains give separate

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Electronic Supplementary Information (ESI) available: Reagents and Instrumentation, Experimental procedures, ¹H spectra. See DOI: 10.1039/x0xx00000x

Scheme 1: The synthesis hexyl- and butylthiophene copolymers with different organometallic functions

Table 1: Overview of the considered combinations of organometallic functions

	Au	Sn	B	Zn
Mg	x	x	(x)	x
Zn	x	x	(x)	
B	x	x		
Sn	x			

signals for their CH₃-end group in ¹H NMR spectroscopy, enabling an easy determination of the polymer composition (Figure S1, ESI).¹⁶ In addition, they are known to randomly copolymerize when bearing the same organometallic function, so the effect of the different organometallic functions is easily detected.^{16,17} The organometallic functions used in this study are (1) Grignard, (2) organozinc, (3) organoboron, (4) organotin, and (5) organogold (Table 1). Although the latter is quite new, Kumada-Tamao Corriu, Negishi, Suzuki-Miyaura and Migita-Kosugi-Stille couplings, respectively, have already been widely used in the synthesis of conjugated polymers.^{1,2,18–25} Recently, the research group of Luscombe also described the controlled synthesis of P3HT using the aurylated monomer with a PdPEPSSI-IPr catalyst, making this monomer very suited for the current study.²⁶ Furthermore, it is decided to work with the PdPEPSSI-IPr catalyst throughout, because it already exhibited a wide applicability in the synthesis of P3HT with different organometallic functions.^{25–28}

Compatibility of the Grignard monomer

For this concept to work, it is clear that the monomers may not react with each other prior to the start of the polymerization. Because the organoboron monomer requires the addition of water and base for a proper polymerization, combinations of this monomer with both Grignard and organozinc monomers are not considered. To investigate possible interactions of the Grignard monomer with any of the other candidates, a test reaction was performed in which the different combinations were reacted with benzaldehyde. Grignard compounds are known to be sufficiently reactive to perform a nucleophilic attack on the aldehyde function, resulting in the formation of compound **1** (Scheme 2). However, all other monomers are unable to react in a similar way. Hence, only compound **1** should be formed, and this in equal amounts to the Grignard monomer that was originally present.

Scheme 2: Test to determine the compatibility of the different monomers with the Grignard monomer

Figure 1: possible complex formed when the aurylated monomer is combined with the Grignard monomer

The combination of the Grignard reagent with the organozinc monomer was previously examined by our research group, and showed not only the formation of **1**, but also equal amounts of **2**.¹⁶ In this study, a similar observation was made when the stannylated compound was combined with the Grignard reagent, although slightly longer mixing (10 minutes) at room temperature was required. Nevertheless, it clearly indicates that exchange occurs between the monomers.

When the Grignard monomer was combined with the aurylated compound, a different observation was made, being that no coupled product was formed at all. Only when an excess of the Grignard monomer was used, compound **1** was formed. A possible explanation is the formation of a larger complex, comparable to the formation of organocuprates from Grignard reagents (Figure 1).^{29,30} Since both copper and gold are group 11 elements, such a similarity would not be surprising. Furthermore, it explains the observations, as the formed organogold complex would not be sufficiently reactive for reaction with the benzaldehyde. To further confirm this hypothesis, ¹H NMR spectra were recorded of both monomers, and their mixture (Figure S5, ESI). The spectrum of the mixture indeed shows the disappearance of the original components and the formation of a new species.

Copolymerization using different organometallic functions

The copolymers were synthesised by mixing the monomers for a few minutes, after which the PdPEPSSI-IPr catalyst was added. Since the organogold monomer requires an elevated temperature of 60°C to obtain a proper polymerization rate, and for solubility reasons, this temperature was used for all copolymerizations. To evaluate the structure of the polymer being formed, the polymer composition was determined at low conversion and compared with the one at full conversion (ESI). Because of the incompatibility of the Grignard and organozinc monomer with the water required for the polymerization of organoboron monomer, combinations of the aforementioned were not considered.

A successful copolymerization of all combinations involving Grignard reagents was achieved, although random poly(3-hexylthiophene-co-3-butylthiophene) was formed every time. Despite the significant difference in reactivity between the

monomers, the observed interactions discussed in the previous paragraph cause a random incorporation of both monomers. A similar observation was made for the organozinc monomer. This monomer was used in a copolymerization with the stannylated monomer on the one hand, and the aurylated monomer on the other. Also in this case, random poly(3-hexylthiophene-co-3-butylthiophene) was formed with both combinations, again suggesting interaction between the monomers. Nevertheless, the formation of a larger organogold complex is not observed in this case (Figure S6, ESI).

Next, the combinations with the organoboron monomer were considered. The two remaining combinations are (1) the organoboron monomer with the organotin monomer and (2) the organoboron monomer with the aurylated monomer. To enable the polymerization of the organoboron monomer, 3 equivalents of H_2O and 3 equivalents of K_3PO_4 were added to these copolymerizations. Although both monomers were incorporated during the polymerization, again no gradient was observed for either of these combinations. To investigate possible interactions between the monomers, a ^1H NMR spectrum was recorded of a thiophene with a B(pin) functional group, together with 3 eq of H_2O and K_3PO_4 , after which also thiophene with a trimethyltin functionality or thiophene with an organogold functionality was added and spectra were recorded of these mixtures (Figure S7 and S8, ESI). Simple thiophene rings were used instead of the actual monomers, because this enabled us to also add the PdPEPPSI-IPr catalyst to the NMR tube in a next step, in order to mimic the actual polymerization even more closely and exclude any possible mediation of the catalyst to the interaction. However, the spectra with and without the catalyst show no interaction of the monomers for both combinations of the organoboron compound.

In conclusion, all combinations discussed so far can be copolymerized successfully, but a random incorporation of both monomers is obtained in all cases.

The gold-tin combination

Homopolymerizations

Finally, the only remaining combination was considered: stannylated and aurylated monomer. Both are known to polymerize in a controlled way using the PdPEPPSI-IPr catalyst. For the aurylated monomer, this is proven at a temperature of 60°C without any additives, the conditions which we also chose to employ.²⁶ However, for the stannylated compound this is only proven at 40°C in the presence of CsF.²⁵ Hence, in a first

Figure 2: Both graphs showing a linear trend for the polymerization of the stannylated monomer with PdPEPPSI-IPr at 60°C indicates that this polymerization is controlled.

Figure 3: Lewis-Mayo plot for the copolymerization of the stannylated and aurylated thiophene monomers with $r_A = 0.20 \pm 0.05$ and $r_B = 1.7 \pm 0.2$. The aurylated monomer is incorporated preferentially at low conversion. The polymerisations were repeated three times.

step, the controlled character of this polymerization was verified at 60°C without CsF. It was found that, also under these conditions, a controlled polymerization was achieved, as evidenced by the graphs showing $\ln [M]_0/[M]$ vs time, with $[M]$ being the monomer concentration, and $\bar{M}_n$ vs conversion (Figure 2). These graphs prove the absence of termination and transfer reactions, respectively.

Copolymerization

Contrary to the previous results, the ^1H NMR spectra of the copolymers at low conversion show that a preferential incorporation of one monomer does occur when the organogold and organotin monomers are copolymerized (Figure 3). As evidenced by the Lewis-Mayo plot, it is observed that the organogold monomer is built in more rapidly at the beginning of the polymerization, which can be explained by the favourable gold-palladium interactions.^{31–37} As a consequence, a considerable amount of AuPtBu_3Br is released into the reaction mixture at quite low conversions, which could possibly transmetallate with the stannylated butylthiophene monomer.³¹ To investigate whether this reaction is actually occurring, AuPtBu_3Br was synthesized by reacting AuPtBu_3Cl with KBr in acetone.³⁸ Subsequently, the AuPtBu_3Br was combined with the stannylated monomer in THF-*d*8 and ^1H NMR spectra were recorded after mixing at room temperature and at various time intervals after heating to 60°C . It was found that both species can coexist without any interaction, even after prolonged heating (Figure S9, ESI). Hence, the mechanism of the gradient copolymerization is not associated with transmetalation between stannylated monomer and AuPtBu_3Br , but with the polymerization rate of each monomer. Based on the Lewis-Mayo plot, the difference in reactivity between both monomers is suited to obtain gradient copolymers. However, a controlled chain growth polymerization is required in order to obtain a uniform batch of gradient copolymers. Hence, the controlled character of the copolymerization was verified by (1) performing a chain

Figure 2: The molar mass of the obtained polymers does not correspond to the aimed degree of polymerization $[M]/[I]$, indicating that this polymerization is not controlled

extension experiment and (2) plotting the ratio of monomer to initiator versus the obtained molar mass, which should show a linear increase. However, both experiments indicate that the polymerization is not controlled. First of all, no chain extension could be achieved after adding a second batch of monomer to the polymerization. Second, the degree of polymerization is not determined by the ratio of monomer to initiator, as shown in Figure 2. Strangely, the obtained polymers are much longer than was aimed for based on the monomer to initiator ratio. Hence, transfer reactions are not responsible for this observation, as they would result in shorter polymer chains. Termination reactions typically lead to a fraction of polymer chains with twice the chain length (disproportionation), or alternatively also to shorter polymer chains (often related to dissociation of the catalyst), neither of which are observed. Also the occurrence of a step-growth polymerization does not explain this observation, because the stoichiometric imbalance induced by the use of a Pd(II) catalyst would result in lower molar masses, especially for smaller $[M]/[I]$. Hence, the actual mechanism is difficult to resolve and probably a combination of different processes. It is concluded that the copolymerization is not controlled and a mixture of various copolymers will be formed.

Influence of CsF and change in temperature

Influence of CsF

In this section, it is investigated whether the addition of CsF can influence the copolymerizations of the tin-, boron-, and gold-functionalized monomers. It has been reported that the addition of a fluoride source can facilitate both Migita-Kosugi-Stille and Suzuki-Miyaura couplings, and CsF is often found to be the most efficient source.^{39–42} Consequently, the addition of CsF can influence the gradient in these three copolymerizations.

Hence, the copolymerizations are repeated with two equivalents of CsF added to the reaction mixture. Again, the polymers are analysed at low conversion and at full conversion to verify whether the gradient is altered (Table 2).

It can be seen that the situation remains similar for the combinations with gold: a random incorporation of both monomers (no change in composition between low and high conversion) is still obtained for the boron-gold combination, while the gradient remains similar for the gold-tin combination. However, a gradient is observed for the boron-tin combination when CsF is added, while this was not the case without CsF. The boron-functionalized monomer is now preferentially incorporated at low conversion, suggesting that the addition of CsF accelerates the transmetalation of this monomer more substantially. Hence, also the boron-tin combination can lead to the formation of a gradient copolymer if CsF is added. It is remarkable that this effect is not observed for the combination with the gold-functionalized monomer.

Influence of the temperature

Next, the influence of the temperature is investigated by repeating the three copolymerizations involving the tin-, boron-, and gold-functionalized monomers at a lower temperature (40°C). However, the reduced solubility at 40°C causes the polymers to precipitate before they can reach full conversion. The presence of the smaller butyl side-chains on approximately half of the thiophene monomers diminishes the solubility compared to poly(3-hexylthiophene). The quenches at low conversion again show a random incorporation of both monomers for the Au/B combination, a preferential incorporation of the boron-functionalized monomer in the B/Sn combination and a preferential incorporation of the gold-functionalized monomer for the Au/Sn polymerization. Unfortunately, the change in polymer composition at full conversion cannot be determined due to the precipitation.

Conclusion

The effect of changing the organometallic function of one of both monomers in a copolymerization is investigated. More specifically, hexyl- and butylthiophene are copolymerized using an organomagnesium, organozinc, organoboron, organotin, or organogold functionality. While hexyl- and butylthiophene copolymerize randomly in a CTCP polymerization without any special precautions, the different organometallic functions can affect the reactivity of the monomers and, hence, the structure of the copolymer. However, the Grignard monomer is shown to react with all other monomers, which does not compromise a

Table 2: Overview of the effect of CsF on the polymer composition. While the situation remains similar with our without CsF for the Au+B and Au+Sn combinations, a gradient structure is obtained for the B+Sn combination when CsF is added, while this was not the case without CsF.

Combination	Without CsF		With CsF	
	Low conversion	High conversion	Low conversion	High conversion
Au + B	45 % Au	48 % Au	58 % Au	56 % Au
Au + Sn	71 % Au	50 % Au	77 % Au	57 % Au
B + Sn	49 % B	50 % B	70 % B	53 % B

successful copolymerization, but results in the formation of a random copolymer despite the significant difference in reactivity between the monomers. Also the combinations including organozinc and organoboron monomers are found to form random copolymers of hexyl- and butylthiophene. Hence, the only remaining combination is the one where an organogold and an organotin monomer are combined. For this combination, it is found that the aurylated monomer is preferentially incorporated at low conversions. Consequently, a gradient is observed in the monomer consumption. However, because the polymerization is not controlled, a mixture of various copolymers will be formed instead of a well-defined batch of gradient copolymers. While the addition of CsF to the copolymerizations had no effect for the Au/Sn and Au/B combinations, a preferential incorporation of the boron-functionalized monomer at low conversion was observed for the B/Sn combination, while a random copolymer was obtained in the absence of CsF. The study on the effect of lowering the temperature was severely complicated by the precipitation of the polymers before they could reach full conversion. Nevertheless, the successful tuning of the monomer incorporation in these copolymerizations confirms the viability of this novel concept.

Acknowledgements

We like to acknowledge Onderzoeksfonds K.U.Leuven/Research Fund K.U.Leuven and the Fund for Scientific Research (FWO Vlaanderen) for financial support. T.H. is a doctoral fellow of the Fund for Scientific Research (FWO Vlaanderen). Prof. Pascal Gerbaux and prof. Julien De Winter are acknowledged for the MALDI-ToF spectrum.

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