The Controlled Polymerization of a Cyclopentadithiophene-Phenylene Alternating Copolymer

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Abstract: In this manuscript, the new conjugated poly(4,4-bis(2-ethylhexyl)cyclopentadithiophene-*alt-p*-phenylene) (PCPDTPP) has been synthesized in a controlled way via catalyst transfer condensative polymerization (CTCP) of the corresponding bi-aryl monomer. Therefore, a series of Ni-catalysts as well as (new) Pd-PEPPSI catalysts were employed in different Kumada CTCPs (KCTCPs) and Negishi CTCPs (NCTCPs). A series of tests confirmed the absence of undesired transfer and termination reactions and hence, the controlled character of the chain-growth polymerization with Ni(dppe)Cl₂ as catalyst. This resulted in polymers with low dispersities ($\mathcal{D} = 1.2$), $\bar{M}_n$ of 33 kDa and relatively good end-group control. Furthermore, formation of PCPDTPP-*b*-poly(3-octylthiophene) (P3OT) block

copolymers was possible. Via optical analysis and DSC measurements, we demonstrated that the conjugated alternating PCPDTPP copolymer is an amorphous, strongly fluorescent polymer with a fluorescence quantum yield (ϕ_f) of 58% in chloroform.

INTRODUCTION

Conjugated polymers (CP) have already proven to be interesting materials for different optoelectronic applications, such as photovoltaic applications¹⁻³ and organic light-emitting diodes^{4,5}. In this field, tailoring the bandgap appears to be crucial. In particular, low-bandgap π -conjugated polymers show good performances for these optoelectronic applications.⁶⁻¹³ An interesting strategy to obtain these low bandgap materials is the creation of donor-acceptor (D-A) π -conjugated alternating copolymers. These alternating copolymers are typically prepared by a polycondensation of A₂ and B₂ monomers. This polymerization proceeds in a step-growth manner, which is notorious for low and unpredictable molar masses, high dispersities and poor end-group fidelity.

After Yokozawa and McCullough independently discovered the living polymerization of poly(3-hexylthiophene) (P3HT)^{14,15}, the field of conjugated polymers underwent a rapid evolution. In contrast to step-growth polymerization, living chain-growth polymerizations can result in a polymer with controlled molar mass and low dispersity, crucial for good polymer performances. The most widely used method to obtain a controlled chain-growth polymerization is CTCP. In this method the control over the polymerization relies on the association of the catalyst to the π -conjugated polymer backbone.¹⁵⁻²³ Since the complexation is different for electron poor and electron rich monomers, synthesizing alternating copolymers from A-B monomers via a controlled chain-growth mechanism remains a challenge. More precisely, the catalyst will be trapped by the most electron rich unit and polymerization will not take place. Nevertheless, the research group of Huck obtained poly(9,9'-dioctylfluorene-

alt-benzothiadiazole) (pF8BT) in this way via a Suzuki condensation polymerization of the 9,9'-dioctylfluorene-*alt*-benzothiadiazole (F8BT) monomer.²⁴ However, only moderate molar masses were obtained. Bielawski and coworkers were the first group to obtain poly(thiophene-*alt*-*p*-phenylene) (PTPP) via a KCTCP of the corresponding bi-aryl monomer with Ni(dppp)Cl₂.²⁵ The same research group synthesized in a similar way poly(5,6-difluorobenzotriazole-*alt*-4-hexylthiophene) (PFBTzHT) with narrow dispersities.²⁶ Also Noonan and coworkers were able to obtain alternating conjugated copolymers via the KCTCP of bi-aryl^{27,28} and tri-aryl²⁸ monomers. Another approach to achieve alternating polymers via the polymerization of bi-aryl monomers, relies on transition-metal-free controlled polymerization.²⁹ Although control over the molar mass and a low dispersity can be obtained, chain extension and block copolymerization remains a problem. Furthermore, this method cannot be applied on a large monomer range.

Although a lot of progress has been made in the synthesis of alternating conjugated copolymers, the diversity of monomers that can be copolymerized in a controlled way remains very limited. Since the control over the polymerization relies on the association of the catalyst to the π -conjugated polymer backbone, finding the appropriate catalyst remains a crucial step if one wants to broaden this monomer scope. Therefore, there is since the last decade an ongoing search for more performing catalysts. An important approach to influence the catalytic activity, is to modify the electronic and steric properties of the ligands of the catalyst. The research group of McNeil discovered that electron rich ligands promote the chain-growth pathway.³⁰ Furthermore, they experienced that strongly hindered ligands can interfere with the chain-growth pathway, while unhindered ligands can lead to an easy catalyst decomposition.³¹ Besides the typically used catalysts with phosphine-based ligands, also NHC-containing catalysts (NHC = *N*-heterocyclic carbenes) have proven their efficiency. The steric and electronic properties of these NHC-catalysts can easily be varied. Many synthetic pathways

using well-known heterocyclic chemistry exist for the preparation of NHCs and moreover both steric and electronic parameters can be varied independently.³²

In this manuscript the synthesis of a new AB-type alternating CP via KCTCP and NCTCP of the corresponding bi-aryl monomer is described by employing a series of well-known standard Ni-catalysts and (new) Pd-PEPPSI-catalysts (Scheme 1).

Scheme 1. Schematic visualization of the KCTCP and NCTCP of the CPDTPP bi-aryl monomer.

The bi-aryl monomer which is polymerized, is a combination of cyclopentadithiophene and phenylene (CPDTPP). Since the thiophene-phenylene bi-aryl monomer has already been polymerized in a controlled way by the research groups of Bielawski²⁵ and ours³³, and because the cyclopentadithiophene donor unit has a relatively large molecular length, we chose this CPDTPP monomer as a next step in this challenging research. Since a catalyst can dissociate from the polymer backbone while ring-walking over a long monomer, it becomes more challenging to polymerize such monomers in a controlled way. Furthermore, cyclopentadithiophene is used a lot as a building block in D-A polymers for optoelectronic applications. Since KCTCP remains one of the most used CTCPs and NCTCP allows the use of a broader scope of functional groups, both polymerization systems were chosen. For KCTCP, standard catalysts such as Ni(dppp)Cl₂, Ni(dppe)Cl₂ and Ni(PPh₃)(*i*Pr)Cl₂ are tested. For NCTCP, the standard [Pd-PEPPSI-(*i*Pr)Cl₂] catalyst is tested, as well as a series of (new) Pd-PEPPSI catalysts with different electronic and steric properties (Figure 1).

Figure 1. Overview of the different Ni-catalysts and Pd-PEPPSI catalysts.

RESULTS AND DISCUSSION

Synthesis of the precursor monomer. The synthesis of the precursor monomer **4** is shown in Scheme 2. Cyclopentadithiophene **1** was synthesized according to literature procedure.^{34,35} After coupling of stannylated compound **2** to 1-bromo-4-iodobenzene via a Stille coupling, compound **3** was obtained after purification. Finally, iodination with I_2 and PhI(OAc)_2 resulted in the final precursor monomer **4**. Since it is not possible to separate the iodinated product from the non-iodinated one, full conversion was required.

Scheme 2. Schematic visualization of the synthesis of the CPDTPP bi-aryl precursor monomer **4**.

Synthesis of the catalysts. Nine different catalysts were synthesized. Apart from the standard Ni-catalysts and Pd-PEPPSI catalysts, also new Pd-PEPPSI catalysts were prepared. For this purpose [Pd-PEPPSI-(*i*Pr*)Cl₂] has been chosen because of its increased steric hindrance, which can result in a more stable and performant catalyst, as has already been proven for certain coupling reactions.³⁶ Taken into account that the catalytic activity can be influenced by modification of the electronic and steric properties, the [Pd-PEPPSI-(Anisole)Cl₂] catalyst was designed. First, phenyl groups were placed in the *ortho*-position in order to create a new steric environment compared to the other Pd-PEPPSI catalysts. Second, methoxy-groups were placed in the *para*-positions of the phenyl groups to increase the electronic density, which can result in a stronger interaction with the polymer backbone.³² Finally, the [Pd-PEPPSI-(*i*Pr-bimy)Cl₂] catalyst was designed because of its lower sterically demanding *N*-groups and different electronic properties compared to the other Pd-PEPPSI catalyst. Furthermore, this NHC ligand has already proven its utility in other Pd-catalyzed reactions.³⁷ All Ni-catalysts, [Pd-PEPPSI-(*i*Pr)Cl₂], [Pd-PEPPSI-(*S*/*i*Pr)Cl₂] and [Pd-PEPPSI-(*i*Pent)Cl₂] were purchased from Sigma-Aldrich, TCI and Acros. The [Pd-PEPPSI-(*i*Pr*)Cl₂] catalyst was prepared according to literature procedure.³⁶ For the synthesis of the [Pd-PEPPSI-(Anisole)Cl₂] catalyst (Scheme 3A), amine **7** was first synthesized from the coupling of 4-methoxyphenylboronic acid and 2,6-

dibromoaniline with $\text{Pd}(\text{PPh}_3)_4$ and Cs_2CO_3 . Amine **7** was transformed into the corresponding diimine **8** via reaction with glyoxal in the presence of formic acid and MgSO_4 . Reaction of the diimine with paraformaldehyde, ZnCl_2 and HCl , resulted in the corresponding NHC-salt **9**. In a last step **9** was added to PdCl_2 , K_2CO_3 and 3-chloropyridine, which resulted in the desired $[\text{Pd-PEPPSI-(Anisole)Cl}_2]$ catalyst. For the synthesis of the $[\text{Pd-PEPPSI-(}i\text{Pr-bimy)Cl}_2]$ catalyst (Scheme 3B), NHC-salt **10** was prepared as reported in literature, and reacted in a last step with PdCl_2 , K_2CO_3 and 3-chloropyridine.³⁷ The synthetic pathway starting from the amine to form the Pd-PEPPSI catalyst as end product, is a standard procedure and can be applied on a broad variety of ligands.³⁸⁻⁴¹

Scheme 3. Synthetic pathway to form (A) $[\text{Pd-PEPPSI-(Anisole)Cl}_2]$ and (B) $[\text{Pd-PEPPSI-(}i\text{Pr-bimy)Cl}_2]$

Polymerization via a chain-growth mechanism. Precursor monomer **4** was polymerized via different KCTCPs as well as NCTCPs, as shown in Scheme 4. Before polymerization, **4** was transformed *in situ* into the desired monomers. In a first step, **4** underwent a Grignard Metathesis (GRIM) reaction with *i*PrMgCl·LiCl at 0° C for 40 minutes, in order to obtain monomer **5** for KCTCP. For NCTCP monomer **5** underwent an extra transmetalation step for 15 minutes at 0° C with ZnCl₂. This resulted in the final monomer **6**. A small amount of the GRIM reaction was quenched with H₂O in order to determine the amount of monomer formed (>99% - see supporting information S24). For KCTCP, dry THF was added to the three Ni-catalysts (10 mol%), whereafter monomer **5** was added for a polymerization time of 60 minutes. The same was done for the different NCTCPs, but with **6** as monomer and with the different Pd-PEPPSI catalysts (10 mol%). After 60 minutes the polymerization reactions were terminated with acidified (HCl) THF, in order to prevent disproportionation⁴², and samples **P1-P9** were obtained.

Scheme 4. Synthesis of samples **P1-P3** via KCTCP and **P4-P9** via NCTCP.

using the three different Ni-catalysts, rendering sample **P1-P3** (Table 1). **P2**, which was polymerized with Ni(dppe)Cl₂, clearly showed better results than **P1** and **P3**, obtained with respectively Ni(dppp)Cl₂ and Ni(PPh₃)(*i*Pr)Cl₂ as catalyst. While for **P1** and **P3** a mix of polymers and oligomers was obtained with broad dispersities and a monomer conversion of respectively 94% and 95%, **P2** resulted in a monomodal polymer mixture with a $\bar{M}_n$ of 25.7 kg.mol⁻¹, a low dispersity of 1.2 and a monomer conversion of 98%. For the different NCTCPs, polymer material was obtained with [Pd-PEPPSI-(*i*Pr)-Cl₂] and [Pd-PEPPSI-(*i*Pent)-Cl₂] as catalysts (**P4-P9** – Table 1). The polymerization of monomer **6** with both catalysts, resulted in monomodal polymer mixtures **P4** and **P6** with a monomer conversion of 98%. Although polymers with relatively high $\bar{M}_n$ were achieved, higher dispersities of 1.7 were observed. Polymerization with [Pd-PEPPSI-(Anisole)-Cl₂] resulted in a mix of oligomers with a small amount of polymer material, a broad dispersity of 2.8 and a monomer conversion of 75%. Polymerization with [Pd-PEPPSI-(*S*/Pr)-Cl₂] and [Pd-PEPPSI-(*i*Pr-bimy)-Cl₂] resulted in oligomers with a monomer conversion of respectively 83% and 39% while [Pd-PEPPSI-(*i*Pr*)-Cl₂] resulted in a small amount of dimers with a monomer conversion of 25%.

Table 1. Overview of the different polymerizations. $\bar{M}_n$ and Đ were measured via GPC in THF at 30 °C and with polystyrene as standards.

Entry	Monomer	Catalyst	Polymer	$\bar{M}_n$ (kg. mol ⁻¹)	Đ
1	5	Ni(dppp)Cl ₂	P1	6.4	2.1
2	5	Ni(dppe)Cl ₂	P2	25.7	1.2
3	5	Ni(PPh ₃)(<i>i</i> Pr)Cl ₂	P3	2.3	1.8
4	6	[Pd-PEPPSI-(<i>i</i> Pr)-Cl ₂]	P4	9.5	1.7
5	6	[Pd-PEPPSI-(<i>S</i> /Pr)-Cl ₂]	P5	<i>o</i>	<i>o</i>
6	6	[Pd-PEPPSI-(<i>i</i> Pent)-Cl ₂]	P6	24.7	1.7
7	6	[Pd-PEPPSI-(<i>i</i> Pr*)-Cl ₂]	P7	<i>d</i>	<i>d</i>
8	6	[Pd-PEPPSI-(anisole)-Cl ₂]	P8	3.2	2.8
9	6	[Pd-PEPPSI-(<i>i</i> Pr-bimy)-Cl ₂]	P9	<i>o</i>	<i>o</i>

d: only dimers were formed, *o*: only oligomers were formed

Analysis of the controlled character of the polymerizations. Since only entries 2, 4 and 6 resulted in polymers with a monomodal distribution, only these combinations were further investigated for their controlled character (GPC spectra see supporting information S27). In order to do so, two different experiments were performed. In a first experiment at least five polymers are synthesized with different monomer over initiator ratios ([M]/[In]). If undesired transfer reactions are absent, a linear relationship between the molar mass and this ratio should be obtained for an equal monomer conversion. The second experiment consists of a chain extension experiment to determine if termination reactions are present or not. In the case of a controlled polymerization no termination should be present. Considering that organo-zinc compounds are, in contrast to organo-magnesium compounds, compatible with more functional groups and therefore more desired, the experiments were first applied on the NCTCPs of monomer **6** with the [Pd-PEPPSI-(*i*Pr)-Cl₂] and the [Pd-PEPPSI-(*i*Pent)-Cl₂] catalyst. For both series five different polymerizations were performed (**P10-P19**, supporting information S12). From Figure 2 it is clear that no linear relationship between the molar mass and the monomer

over initiator ratio is obtained for both catalysts. [Pd-PEPPSI-(*i*Pr)-Cl₂] resulted for the lower monomer over initiator ratio in polymer material with too high molar masses compared to the theoretical molar masses. For [Pd-PEPPSI-(*i*Pent)-Cl₂] polymers were obtained with molar masses higher than the molar masses obtained with [Pd-PEPPSI-(*i*Pr)-Cl₂] for a same mol% and higher than the expected theoretical values. Since it is already evident that these NCTCPs are not controlled, the chain extension was not performed. For the KCTCP of monomer **5** with the Ni(dppe)Cl₂ catalyst, six different $[M]/[In]$ ratios were polymerized (**P20-P25**, supporting information S12). Since solubility problems can arise for high molar masses, only monomer over initiator ratios until 20 were chosen. A same monomer conversion of 98% for all polymerizations was obtained. From Figure 3a it is clear that a linear relation between the molar mass and $[M]/[In]$ is present, indicating that no undesired transfer reactions took place at least for a degree of polymerization up to 20. A dispersity of 1.2 was obtained for all polymers. However, the molar masses observed with GPC are much higher than the expected theoretical values. Also the chain extension experiment was performed, by polymerizing two blocks with a same degree of polymerization (polymers **P26-P27**, supporting information S14). Prior to the chain extension experiment, the polymerization growth was monitored in function of time. This is necessary since the second monomer should only be added after the first block stopped growing (supporting information S16). The chain extension was done by adding the second batch of monomer 30 minutes after the addition of the first monomer. As shown in Figure 3b, all polymer chains further increased in molar mass, indicating that the polymerization occurred without termination. Furthermore, MALDI-ToF of polymer sample **P2** was recorded. Since mainly Br/H terminated chains are present, a relatively good control over the end-groups is obtained (supporting information S27). From above experiments it can be concluded that we are able to synthesize the PCPDTPP alternating copolymer in a controlled way with relatively good end-group control via KCTCP and with Ni(dppe)Cl₂ as catalyst.

Figure 2. $\bar{M}_n$ plotted as a function of $[M]/[In]$ for the polymerization of monomer **6** with $[Pd-PEPPSI-(iPr)-Cl_2]$ and $[Pd-PEPPSI-(iPent)-Cl_2]$ as catalysts.

Figure 3. (a) $\bar{M}_n$ plotted as a function of $[M]/[In]$ for the polymerization of monomer **5** with $Ni(dppe)Cl_2$; (b) chain extension experiment of monomer **5** with $Ni(dppe)Cl_2$. The GPC results are plotted before (solid line) and after (dashed line) chain extension.

Block copolymerization. As the polymerization of the CPDTPP monomer **5** with $Ni(dppe)Cl_2$ as catalyst is a controlled chain-growth polymerization, the synthesis of block copolymers with poly(3-alkylthiophenes) (P3ATs) can be considered. Therefore, the synthesis of PCPDTPP-*b*-P3AT and P3AT-*b*-PCPDTPP (**P30**, **P33**, see supporting information S14) was attempted. The

block copolymerizations were performed with the external *o*-tolyl-Ni(dppe)Br initiator in order exclusively to obtain AB block copolymers instead of a mixture of AB and BAB block copolymers. In order to verify whether the first block as well as the block copolymer polymerized successfully, a quench was taken of the first block after which the polymer solution was separated in two portions. The first part underwent a chain extension with the same monomer to confirm that the first block was indeed still living. The other portion was extended with the other monomer. All samples were analyzed with GPC at a wavelength of 425 nm, the absorption maximum of the thiophene block, and 520 nm, the absorption maximum of the PCPDTPP block. Starting from the polymerization of CPDTPP (Figure 4), a monomodal peak was obtained with a dispersity of 1.3 (**P28**). Since it was proven that no transfer and termination reactions occur, the slightly higher $\bar{D}$ indicates that the initiation is slower than the propagation. Extension with the same monomer was as expected successful, indicating that the first block was still living (**P29**). When the thiophene monomer was added in order to form block copolymer **P30**, also an increase in molar mass was observed. At a wavelength of 425 nm as well as 520 nm, a monomodal peak was obtained, proving that block copolymerization from PCPDTPP and P3OT was successful. Starting from the polymerization of the thiophene monomer (Figure 5), P3OT was obtained with a $\bar{D}$ of 1.1 (**P31**). Also here the successful chain extension indicated that the first block was still living (**P32**). However, when CPDTPP was added to P3OT in order to form block copolymer **P33**, overlap of the P3OT peak with a broader peak was obtained, when measuring at 425 nm. This observation is explained by a fast second propagation of PCPDTPP and a slow re-initiation and is in line with the results of the PCPDTPP homopolymerization. Proper block copolymerization is therefore not possible when starting from thiophene. Since P3AT hardly absorbs at 520 nm in comparison to PCPDTPP, only a broad peak is visible instead of two.

Figure 4. GPC results of the synthesis of PCPDTTP-*b*-P3OT.

Figure 5. GPC results of the synthesis of P3OT-*b*-PCPDTTP.

Since an external initiator is used, end-group analysis by ^1H NMR becomes possible. As shown in Figure 6 for **P30**, integration of the separated signals arising from the *o*-tolyl group, the PCPDTTP block and the P3OT block make it possible to determine the degree of

polymerization (DP) of both blocks. For the PCPDTPP and P3OT a DP of respectively 9 and 8 is obtained, which is almost similar to the targeted values of two times a DP of 10.

Figure 6. ^1H NMR analysis of **P30**.

UV-vis and DSC measurements. In order to study the aggregation behavior of the new conjugated alternating copolymer **P2**, a solvatochromism experiment has been performed. Starting from a 100% chloroform solution of **P2**, in which the polymer chains are completely dissolved, non-solvent (methanol) was added stepwise. This was done by the use of a syringe pump with an addition speed of $0.20 \text{ mL} \cdot \text{min}^{-1}$. Upon addition of non-solvent, polymer chains can aggregate, typically visualized by a red shift and the appearance of fine structure. However, when this experiment was applied on polymer **P2** (Figure 7), no red shift took place and no fine structure appeared. CPDT homopolymer does not π -stack, which can be ascribed to an out-of-plane arrangement of the substituents onto the polymer backbone. Alternating copolymers of CPDT with 3,6-dialkoxy-substituted thieno[3,2-b]thiophene stack. Since the combination of both monomers results in enough space for the substituents, the polymer is able to stack.³⁴ This is not the case for the homopolymer or the CPDTPP copolymer in which the phenyl units do not create enough free space. In order to confirm this non-stacking behavior, the polymer powder of **P2** was analyzed using differential scanning calorimetry (DSC) measurements (supporting information S26). The absence of a melting peak ($T < 250 \text{ }^\circ\text{C}$), and

thus crystalline material, confirms the findings from the solvatochromism experiment. Additionally, also UV-vis in film was recorded (see supporting information page S24).

Figure 7. Solvatochromism experiment of polymer **P2** executed by the stepwise addition of MeOH to a chloroform solution of **P2**. ϵ is plotted in function of the wavelength.

Fluorescence measurements. Visually, polymer **P2** is a strongly pink fluorescent polymer. In order to get more information about the fluorescence properties of this conjugated alternating copolymer, fluorescence measurements were recorded and the quantum yield was calculated. Emission spectra of **P2** were recorded in pure chloroform by excitation at 490 nm. The results of five cycles in triplicate are shown in Figure 8, where the mean values with standard deviations are plotted. As shown, $\lambda_{\text{max,em}}$ of polymer **P2** is situated at 590 nm.

Figure 8. Fluorescence spectra of **P2** with excitation at 490 nm. Three times five cycles were recorded. The mean values with standard deviations are plotted in function of the wavelength.

In order to determine the fluorescence quantum yield, fluorescein has been chosen as reference. Furthermore, the quantum yield of a standard P3HT with a DP of 30 has been measured under the same circumstances for comparison. All samples were prepared so that a maximum absorbance of 0.05 was obtained. After recording the emission spectrum of the fluorescein reference in water and polymer sample **P2** and P3HT in chloroform ($\lambda_{\text{ex}} = 475 \text{ nm}$), the fluorescence quantum yield of the polymer sample $\phi_f^{(S)}$ could be calculated (equation 1)⁴³.

$$\phi_f^{(S)} = \phi_f^{(R)} * \left(\frac{A^{(R)} * I^{(S)} * n^{2(S)}}{A^{(S)} * I^{(R)} * n^{2(R)}} \right) \quad (1)$$

With $\phi_f^{(R)}$ the fluorescence quantum yield of the reference, $A^{(R)}$ and $A^{(S)}$ the absorbance of the reference and the polymer sample at the excitation wavelength, $I^{(R)}$ and $I^{(S)}$ the area under the fluorescence spectrum of the reference and the polymer sample, and $n^{2(R)}$ and $n^{2(S)}$ the refractive index of the reference and the polymer sample. For sample **P2** a fluorescence quantum yield ϕ_f of 58% was obtained in chloroform, while the P3HT sample reached a fluorescence quantum yield ϕ_f of 31%. In a 50/50 mixture of chloroform/methanol a fluorescence quantum yield ϕ_f of 1.1% was obtained for **P2** and 0% for P3HT. The low fluorescence quantum yield and hypsochromic shift obtained upon addition of methanol can be related to the formation of H-aggregates. Furthermore, compared to P3AT, a higher fluorescence quantum yield can be obtained by the copolymerization of cyclopentadithiophene and phenylene.

CONCLUSION

In this work, we report the first controlled synthesis of a conjugated alternating copolymer of cyclopentadithiophene and phenylene via the CTCP of the bi-aryl monomer. Although a series of (new) Pd-PEPPSI catalysts have been used in order to obtain a controlled chain-growth

polymerization, only Ni(dppe)Cl₂ resulted via KCTCP in a fully controlled polymerization. The controlled nature of the polymerization was demonstrated by varying the ratio of monomer to initiator, of which the linear relation proved that no transfer reactions took place. An additional successful chain extension experiment proved the absence of termination reactions. Furthermore, a relatively good control over the end-groups is obtained. Since the polymerization proceeds via a controlled chain-growth pathway, it was possible to synthesize PCPDTPP-*b*-P3OT block copolymers. However, synthesis of P3OT-*b*-PCPDTPP was not possible in a proper way due to slow initiation of the second block. Combination of additional optical analysis and DSC measurements demonstrated that the conjugated alternating PCPDTPP copolymer is an amorphous, fluorescent polymer with a fluorescent quantum yield ϕ_f of 58% in chloroform.

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

CTCP, Catalyst Transfer Condensative Polymerization; KCTCP, Kumada Catalyst Transfer Condensative Polymerization; NCTCP, Negishi Catalyst Transfer Condensative Polymerization; $\bar{D}$, Dispersity; $\bar{M}_n$, Number average molar mass; ϕ_f , Fluorescent quantum yield; CP, Conjugated Polymers; D-A, Donor-Acceptor; CPDTPP, cyclopentadithiophene-*para*-phenylene; PCPDTPP, poly(cyclopentadithiophene-*alt-para*-phenylene); GPC, Gel Permeation Chromatography; GRIM, Grignard Metathesis; *i*Pr, isopropyl; THF, Tetrahydrofuran; MALDI-ToF, Matrix-assisted laser desorption/ionization time-of-flight; MeOH, methanol; dppp, bisdiphenylphosphinopropane; dppe, bisdiphenylphosphinoethane; ϵ , absorption coefficient; P3AT, poly(3-alkylthiophene); P3OT, poly(3-octylthiophene); DSC, Differential Scanning Calorimetry; DP, degree of polymerization

ASSOCIATED CONTENT

Supporting Information. Used instrumentation and experimental details as well as ^1H NMR, ^{13}C NMR, MALDI-ToF, GPC spectra, UV-vis spectra, fluorescence spectra, DSC spectra and TGA.

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FOR TABLE OF CONTENTS ONLY

The Controlled Polymerization of a Cyclopentadithiophene-Phenylene Alternating Copolymer

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