

Controlled Polymerization of a Cyclopentadithiophene–Phenylene Alternating Copolymer

Marie-Paule Van Den Eede,[†] Julien De Winter,^{‡,†} Pascal Gerbaux,[‡] and Guy Koeckelberghs^{*,†,†}

[†]Laboratory for Polymer Synthesis, KU Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium

[‡]Organic Synthesis and Mass Spectrometry Laboratory, Interdisciplinary Center for Mass Spectrometry, University of Mons-UMONS, 23 Place du Parc, 7000 Mons, Belgium

Supporting Information

ABSTRACT: The new conjugated poly(4,4-bis(2-ethylhexyl)-cyclopentadithiophene-*alt-p*-phenylene) (PCPDTTP) has been synthesized in a controlled way via catalyst transfer condensative polymerization (CTCP) of the corresponding biaryl monomer. Therefore, a series of Ni catalysts as well as (new) Pd-PEPSI 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(dppf)Cl₂ as catalyst. This resulted in polymers with low dispersities ($D = 1.2$), \bar{M}_n of 33 kDa, and relatively good end-group control. Furthermore, formation of PCPDTTP-*b*-poly(3-octylthiophene) (P3OT) block copolymers was possible. Via optical analysis and DSC measurements, we demonstrated that the conjugated alternating PCPDTTP 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 applications^{1–3} 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.^{6–15} 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} Because 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 co-workers were the first group to obtain poly(thiophene-*alt-p*-phenylene) (PTPP) via a KCTCP of the corresponding biaryl 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 co-workers were able to obtain alternating conjugated copolymers via the KCTCP of biaryl^{27,28} and triaryl²⁸ monomers. Another approach to achieve alternating polymers via the polymerization of biaryl 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 remain 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. Because 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 past decade an ongoing search for more performing

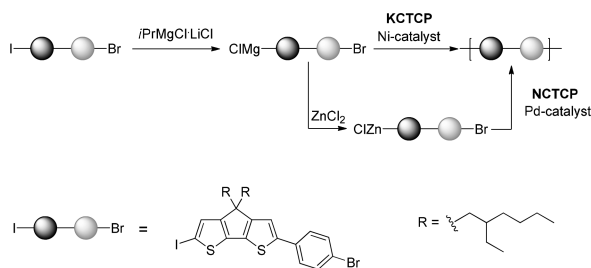
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catalysts. An important approach to influence the catalytic activity is to modify the electronic and steric properties of the ligands of the catalyst. The research group of McNeil discovered that electron-rich ligands promote the chain-growth pathway.³⁰ 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 article the synthesis of a new AB-type alternating CP via KCTCP and NCTCP of the corresponding biaryl 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 Biaryl Monomer



The biaryl monomer, which is polymerized, is a combination of cyclopentadithiophene and phenylene (CPDTPP). Because the thiophene–phenylene biaryl monomer has already been polymerized in a controlled way by the research groups of Bielawski²⁵ and ours,³³ 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. Because 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. Because 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).

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 the 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 I₂ and PhI(OAc)₂ resulted in the final precursor monomer **4**. Because it is not possible to separate the iodinated product from the non-iodinated one, full conversion was required.

Synthesis of the Catalysts. Nine different catalysts were synthesized. Apart from the standard Ni catalysts and Pd-PEPPSI

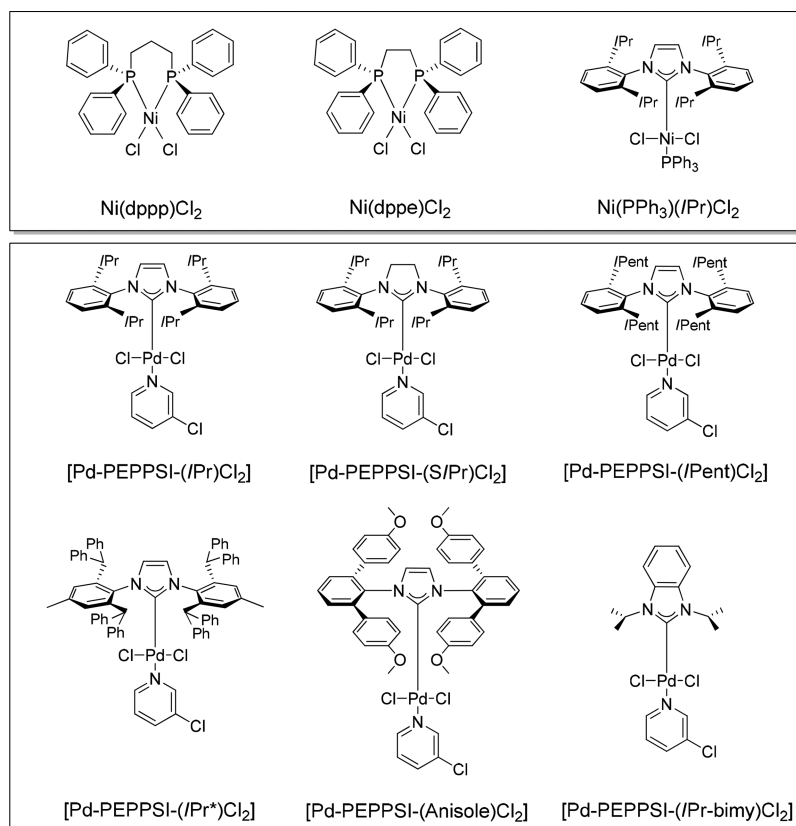
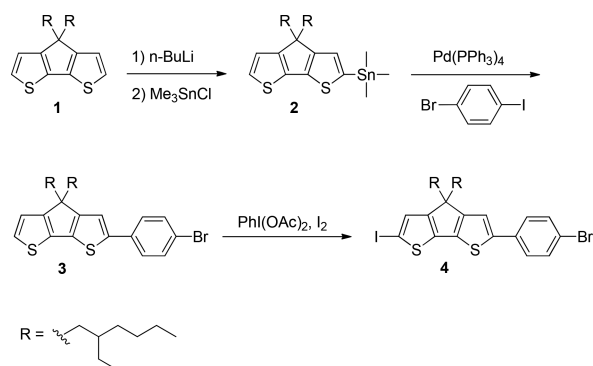


Figure 1. Overview of the different Ni catalysts and Pd-PEPPSI catalysts.

Scheme 2. Schematic Visualization of the Synthesis of the CPDTPP Biaryl Precursor Monomer 4



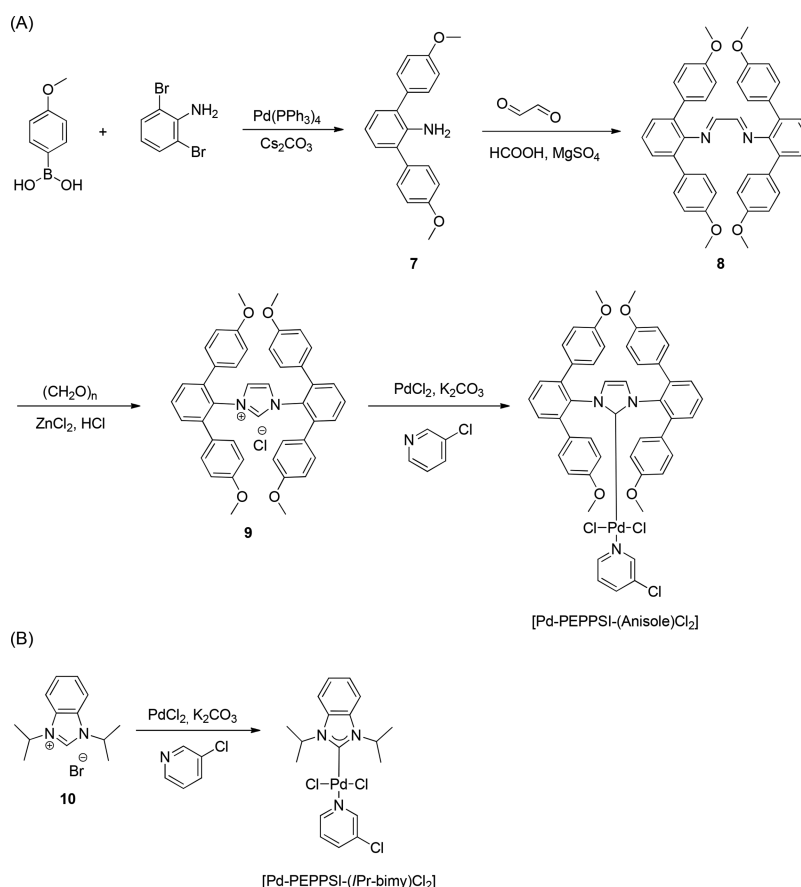
catalysts, also new Pd-PEPPSI catalysts were prepared. For this purpose [Pd-PEPPSI-(*i*Pr*)Cl₂] has been chosen because of its increased steric hindrance, which can result in a more stable and performant catalyst, as has already been proven for certain coupling reactions.³⁶ Taking into account that the 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 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*IPr)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 a 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 Pd(PPh₃)₄ and Cs₂CO₃. Amine 7 was transformed into the corresponding diimine 8 via reaction with glyoxal in the presence of formic acid and MgSO₄. Reaction of the diimine with paraformaldehyde, ZnCl₂, and HCl resulted in the corresponding NHC salt 9. In a last step 9 was added to PdCl₂, K₂CO₃, and 3-chloropyridine, which resulted in the desired [Pd-PEPPSI-(Anisole)Cl₂] catalyst. For the synthesis of the [Pd-PEPPSI-(*i*Pr-bimy)Cl₂] catalyst (Scheme 3B), NHC salt 10 was prepared as reported in the literature and reacted in a last step with PdCl₂, K₂CO₃, 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}

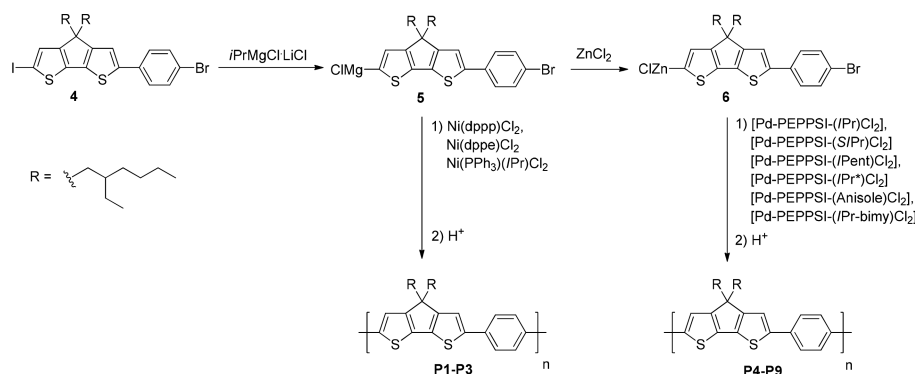
Polymerization via a Chain-Growth Mechanism.

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 min to obtain monomer 5 for KCTCP. For NCTCP monomer 5 underwent an extra

Scheme 3. Synthetic Pathway To Form (A) [Pd-PEPPSI-(Anisole)Cl₂] and (B) [Pd-PEPPSI-(*i*Pr-Bimy)Cl₂]



Scheme 4. Synthesis of Samples P1–P3 via KCTCP and P4–P9 via NCTCP



transmetalation step for 15 min at 0 °C with ZnCl_2 . This resulted in the final monomer **6**. A small amount of the GRIM reaction was quenched with H_2O to determine the amount of monomer formed (>99%; see the Supporting Information, Figure 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 min. The same was done for the different NCTCPs, but with **6** as monomer and with the different Pd-PEPPSI catalysts (10 mol %). After 60 min the polymerization reactions were terminated with acidified (HCl) THF to prevent disproportionation,⁴² and samples **P1–P9** were obtained.

After polymerization, all samples were analyzed using gel permeation chromatography (GPC) to determine the average number molecular weight (\bar{M}_n) and the dispersity (\mathcal{D}). The measurements were performed at 30 °C in THF, and the instrument was calibrated with poly(styrene) standards. The results of all polymerizations are shown in Table 1, and all spectra can be

[Pd-PEPPSI-(*i*Pent)- Cl_2] 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)- Cl_2] 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-(*Si*Pr)- Cl_2] and [Pd-PEPPSI-(*i*Pr-bimy)- Cl_2] resulted in oligomers with a monomer conversion of respectively 83% and 39% while [Pd-PEPPSI-(*i*Pr*)- Cl_2] resulted in a small amount of dimers with a monomer conversion of 25%.

Analysis of the Controlled Character of the Polymerizations. Because only entries 2, 4, and 6 resulted in polymers with a monomodal distribution, only these combinations were further investigated for their controlled character (for GPC spectra see Figure S27). To do so, two different experiments were performed. In a first experiment at least five polymers are synthesized with different monomer over initiator ratios ($[\text{M}]/[\text{In}]$). 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 whether 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)- Cl_2] and the [Pd-PEPPSI-(*i*Pent)- Cl_2] catalyst. For both series five different polymerizations were performed (**P10–P19**, Figure 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)- Cl_2] 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)- Cl_2] polymers were obtained with molar masses higher than the molar masses obtained with [Pd-PEPPSI-(*i*Pr)- Cl_2] for the same mol % and higher than the expected theoretical values. Because 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) Cl_2 catalyst, six different $[\text{M}]/[\text{In}]$ ratios were polymerized (**P20–P25**, Figure S12). Because 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

Table 1. Overview of the Different Polymerizations^a

entry	monomer	catalyst	polymer	\bar{M}_n (kg mol^{-1})	\mathcal{D}
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>Si</i> Pr)- Cl_2]	P5	o	o
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	d	d
8	6	[Pd-PEPPSI-(anisole)- Cl_2]	P8	3.2	2.8
9	6	[Pd-PEPPSI-(<i>i</i> Pr-bimy)- Cl_2]	P9	o	o

^a \bar{M}_n and \mathcal{D} were measured via GPC in THF at 30 °C and with polystyrene as standards. d: only dimers were formed; o: only oligomers were formed.

found in Figure S27. Monomer **5** was polymerized via KCTCP using the three different Ni catalysts, rendering sample **P1–P3** (Table 1). **P2**, which was polymerized with Ni(dppe) Cl_2 , clearly showed better results than **P1** and **P3**, obtained with respectively Ni(dppp) Cl_2 and Ni(PPh₃)(*i*Pr) Cl_2 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)- Cl_2] and

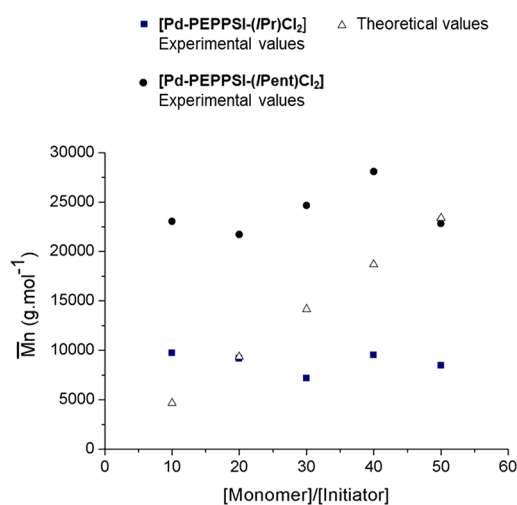


Figure 2. \bar{M}_n plotted as a function of $[M]/[In]$ for the polymerization of monomer 6 with $[Pd-PEPPSI-(iPr)-Cl_2]$ and $[Pd-PEPPSI-(iPent)-Cl_2]$ as catalysts.

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** and **P27**, Figure S14). Prior to the chain extension experiment, the polymerization growth was monitored as a function of time. This is necessary since the second monomer should only be added after the first block stopped growing (Figure S16). The chain extension was done by adding the second batch of monomer 30 min 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. Because mainly Br/H-terminated chains are present, a relatively good control over the end-groups is obtained (Figure S27). From above experiments it can be concluded that we can synthesize the PCPDTTP alternating copolymer in a controlled way with relatively good end-group control via KCTCP and with $Ni(dppe)Cl_2$ as catalyst.

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 PCPDTTP-*b*-P3AT and P3AT-*b*-PCPDTTP (**P30** and **P33**, see Figure 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. 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 PCPDTTP block. Starting from the polymerization of CPDTPP (Figure 4), a monomodal peak was obtained with a dispersity of 1.3 (**P28**). Because 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 to form block copolymer **P30**, also an increase in molar mass was observed. At wavelengths of 425 and 520 nm, a monomodal peak was obtained, proving that block copolymerization from PCPDTTP 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 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 PCPDTTP and a slow reinitiation and is in line with the results of the PCPDTTP homopolymerization. Proper block copolymerization is therefore not possible when starting from thiophene. Because P3AT hardly absorbs at 520 nm in comparison to PCPDTTP, only a broad peak is visible instead of two.

Because 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 makes it

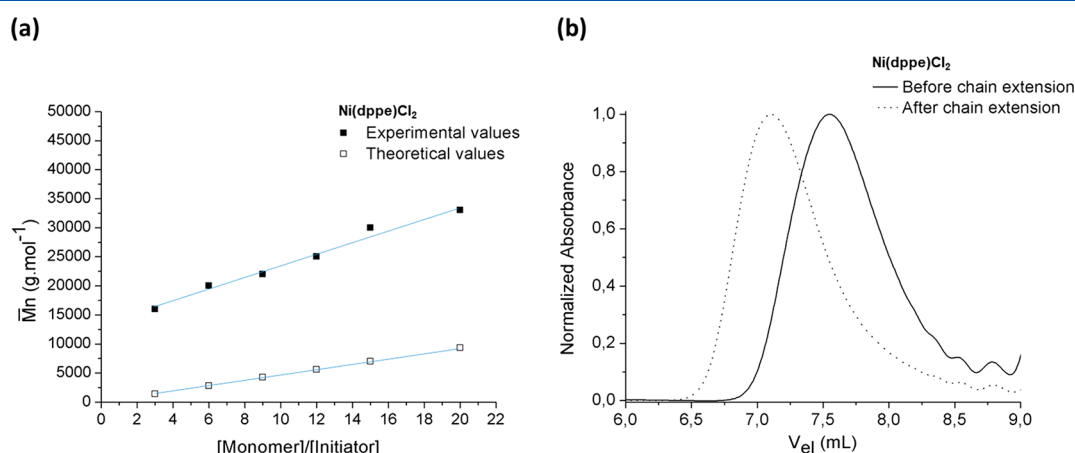


Figure 3. (a) \bar{M}_n plotted as a function of $[M]/[In]$ for the polymerization of monomer 5 with $Ni(dppe)Cl_2$. (b) Chain extension experiment of monomer 5 with $Ni(dppe)Cl_2$. The GPC results are plotted before (solid line) and after (dashed line) chain extension.

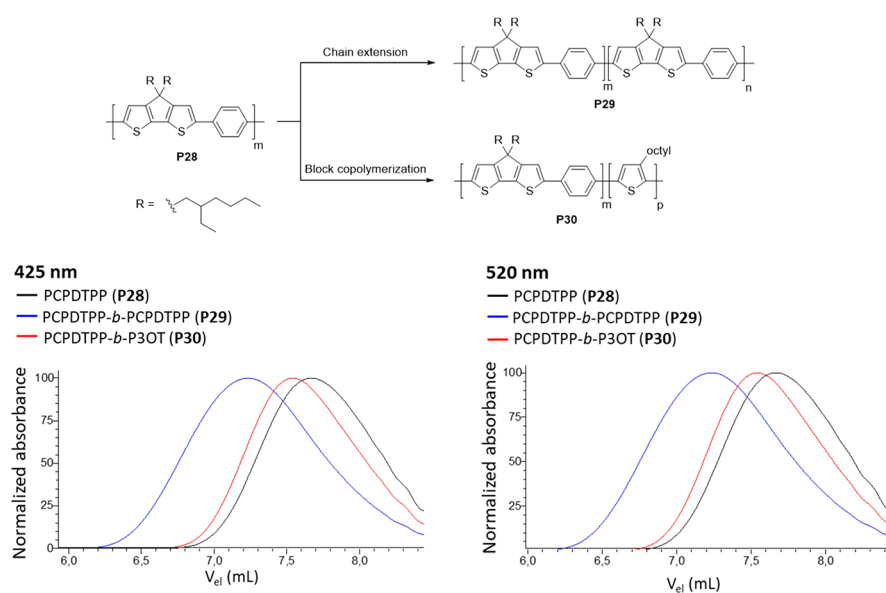


Figure 4. GPC results of the synthesis of PCPDTPP-*b*-P3OT.

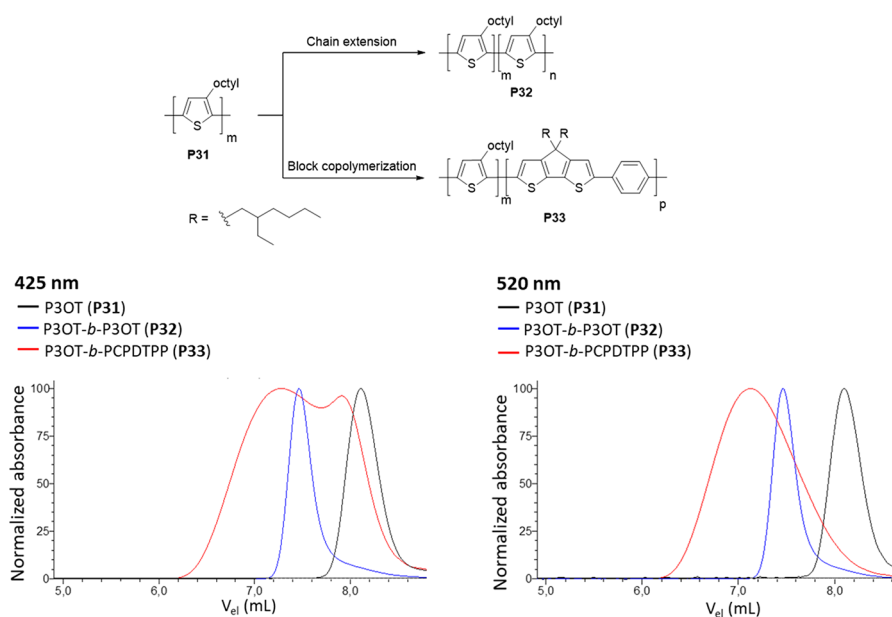


Figure 5. GPC results of the synthesis of P3OT-*b*-PCPDTPP.

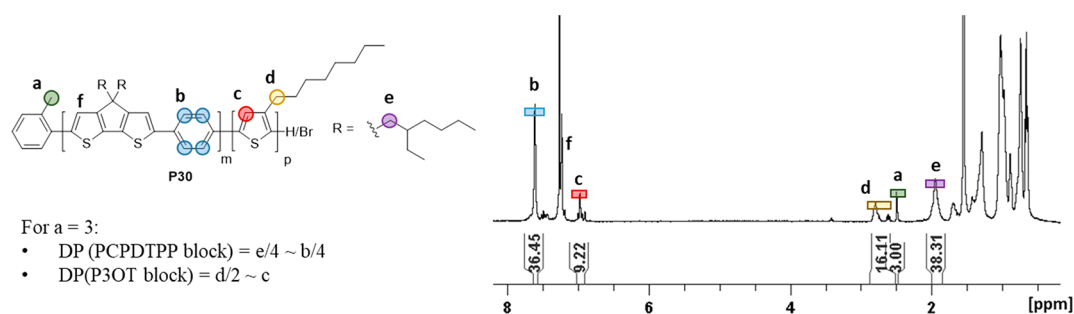


Figure 6. ^1H NMR analysis of P30.

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.

UV–Vis and DSC Measurements. 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, nonsolvent (methanol) was added stepwise. This was done by the use of a syringe pump with an addition speed of 0.20 mL min^{-1} . Upon addition of nonsolvent, 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

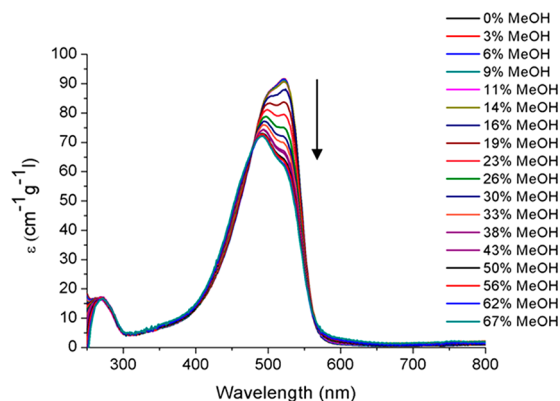


Figure 7. Solvatochromism experiment of polymer **P2** executed by the stepwise addition of MeOH to a chloroform solution of **P2**. ϵ is plotted as a function of the wavelength.

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. Because the combination of both monomers results in enough space for the substituents, the polymer can 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. To confirm this nonstacking behavior, the polymer powder of **P2** was analyzed using differential scanning calorimetry (DSC) measurements (Figure 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 the UV-vis in film was recorded (see Figure S24).

Fluorescence Measurements. Visually, polymer **P2** is a strongly pink fluorescent polymer. 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.

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 samples $\phi_f^{(S)}$ could be calculated (eq 1).⁴³

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

where $\phi_f^{(R)}$ is the fluorescence quantum yield of the reference, $A^{(R)}$ and $A^{(S)}$ are the absorbance of the reference and the

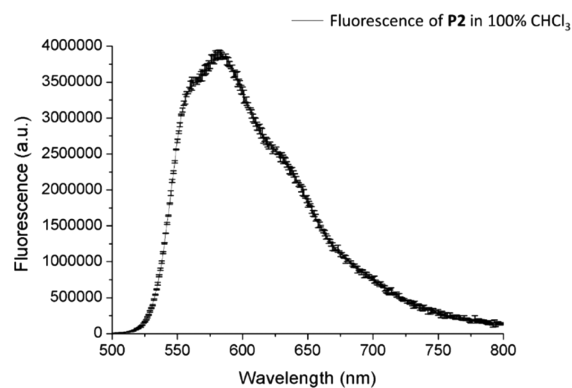


Figure 8. Fluorescence spectra of **P2** with excitation at 490 nm. Three times five cycles were recorded. The mean values with standard deviations are plotted as a function of the wavelength.

polymer sample at the excitation wavelength, $I^{(R)}$ and $I^{(S)}$ are the area under the fluorescence spectrum of the reference and the polymer sample, and $n^{2(R)}$ and $n^{2(S)}$ are 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 biaryl monomer. Although a series of (new) Pd-PEPPSI catalysts have been used 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. Because 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.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b01820.

Used instrumentation and experimental details as well as ¹H NMR, ¹³C NMR, MALDI-ToF, GPC spectra, UV-vis spectra, fluorescence spectra, DSC spectra, and TGA (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail guy.koeckelberghs@kuleuven.be (G.K.).

ORCID

Julien De Winter: 0000-0003-3429-5911

Guy Koeckelberghs: 0000-0003-1412-8454

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; D , dispersity; M_n , number-average molar mass; ϕ_f , fluorescent quantum yield; CP, conjugated polymers; D–A, donor–acceptor; CPDTPP, cyclopentadithiophene–*p*-phenylene; PCPDTPP, poly(cyclopentadithiophene–*alt-p*-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, bis(diphenylphosphino)propane; dppe, bis(diphenylphosphino)ethane; ϵ , absorption coefficient; P3AT, poly(3-alkylthiophene); P3OT, poly(3-octylthiophene); DSC, differential scanning calorimetry; DP, degree of polymerization.

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