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Development of a universal chain-growth polymerization protocol of conjugated polymers: Toward a variety of all-conjugated block-copolymers.

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Abstract

This manuscript reports a universal chain-growth polymerization protocol for conjugated polymers. Herein, the Pd-based catalyst moiety dissociates from the growing active center into the solution and therefore, the controlled chain-growth character is not relying on any specific, system-related complexation, as is the case in polymerization methods reported before. This makes the protocol applicable on a broad range of monomers and, furthermore, also allows an easy one-pot synthesis of block-copolymers by successive monomer addition. A chain-growth

polymerization mechanism for poly(3-hexylthiophene) (P3HT) and poly(9,9-dioctylfluorene) (PF) and all-conjugated block-copolymers of them is presented. Moreover, the sequence of monomer addition in the synthesis of these conjugated block-copolymers is unimportant, which is unique.

Introduction

Conjugated polymers (CPs) remain intensively studied materials as they hold promise as active layers in the field of molecular electronics. The realization of the current and future materials requires tailor-made polymers for stability and electronic optimization reasons (e.g. in organic solar cells). A major break-through in this respect was realized by the groups of McCullough¹⁻² and Yokozawa³⁻⁴ by demonstrating the controlled chain-growth nature of the Ni(dppp)Cl₂ (dppp = 1,3-bis(diphenylphosphino)propane) initiated polymerization of P3ATs. The actual polymerization reaction is a Kumada coupling of 3-alkyl-2-bromo-5-chloromagnesiathiophene. Also other monomers have been polymerized in a chain-growth, sometimes to a certain extent controlled, mechanism.⁵ Apart from the Ni(dppp)- (or Ni(dppe); dppe = 1,2-bis(diphenylphosphino)ethane)-mediated polymerization of CPs, Yokozawa reported the controlled polymerization of poly(fluorene)s, poly(phenylene)s and poly(3-alkylthiophene)s from their monobromo-monoboronic ester-functionalized monomers using PhPd[Pt-Bu₃]Br as an initiator.⁶

In both protocols the controlled chain-growth nature of the polymerization originates from the fact that the catalyst – Ni[dppp], Ni[dppe] or Pd[Pt-Bu₃] – remains complexed to its ‘own’ polymer chain. After reductive elimination, it is intramolecularly transferred to a chain end, where it oxidatively inserts into the C-Br bond. This ‘catalyst transfer’ principle results in a chain-growth polymerization. The fact that the catalyst is not released into the solution protects it from degradation and avoids transfer reactions, which could, for instance, occur when the catalyst

would insert into an aromatic halide bond from monomer, unreacted precursor monomer, etc. Provided that disproportionation of the growing $\text{pol-ML}_2\text{Br}$ and reaction with a Grignard reagent lacking a C-Br bond is prevented, the polymerization is easily turned into a controlled polymerization. Therefore, it can be concluded that the absence of dissociation from the polymer chains results in a chain-growth mechanism and therefore into a controlled polymerization. Endcapping can conveniently be accomplished by reaction with a (functional) Grignard reagent, while all-conjugated block-copolymers can in principle be prepared by successive monomer addition.^{5f, 6b-c, 7}

Unfortunately, the complexation of the Ni[dppp] species to the polymer chain is system-dependent. While it works very well for e.g. P3ATs, it fails for some other systems like for instance $\text{poly(3-alkoxythiophene)}^{5k}$. This does not only pose limitations on the features (predictable molar mass, narrow polydispersities etc.) of the latter polymers, it also renders end-capping of the polymer chains or one-pot block-copolymer formation by simple addition of the second monomer impossible. For block-copolymer formation, it does not even suffice that both blocks can be polymerized via a controlled mechanism, the conditions for both blocks must be compatible as well. As a consequence, the number of all-conjugated block-copolymers composed of electronically different blocks prepared by successive monomer addition remains limited.^{7a, d, g, h, i, j} Moreover, the order of monomer addition is crucial: since the Ni-moiety remains complexed to the polymer chain, efficient block-copolymer formation can only occur if the catalyst has a higher affinity for the second monomer than for the first, since otherwise no or very slow initiation of the second block occurs.⁸ It is clear that a more universal protocol would significantly broaden the scope of conjugated polymers. Here, we present a polymerization protocol of which the controlled chain-growth character does not rely on the association of the catalyst moiety to the conjugated system and is therefore independent of the nature of the monomer/polymer.

Results and Discussion

Concept.

The benefit of the existing protocols, relying on the strong association of the Ni-moiety to the polymer, is that they may lead by the chain-growth mechanism to a controlled polymerization. However, this is also limiting the applicability since the control relies on the system-dependent complexation of the Ni-species to the π -conjugated system. After all, a one pot synthesis of all-conjugated block-copolymers is only feasible when both blocks undergo controlled polymerization under the same conditions. (e.g. with the same catalyst, ligand, additives, etc). A chain-growth mechanism can also be introduced in an alternative way. Yokozawa and coworkers realized a chain-growth polymerization of a poly(amide) starting from A-B functionalized monomers in which the A functionality deactivates the B functionality, preventing a coupling with the A function of another monomer ().⁹ Initiation of the polymerization is performed by a molecule that only bears an active B function. Once the A function of the monomer disappears in the coupling reaction, the B function of the monomer becomes active for coupling and chain-growth is realized. It is important to note that this approach allows a catalyst moiety which can be released from the polymer chain – the chain-growth nature originates from the deactivation of the B function in the A-B substituted monomers. Applied on the formation of block copolymers, it is even advantageous for the catalyst to be released from the polymer chain, because block copolymer formation does not require the catalyst to have a stronger complexation affinity for the second monomer than for the first (see also further).

Applied on the polymerization of conjugated polymers, the A and B functionalities are typically an organometallic and halogen, respectively.¹⁰ The above-mentioned approach therefore requires a catalyst which (i) is easily released from the π -system of the propagating polymer chain, (ii) is stable and does not degrade when free in solution and (iii) undergoes easily oxidative reinsertion in the aromatic C-Br bond on the end of a polymer chain (). To meet with these requirements we

opted for a Pd-catalyst containing a very efficient Buchwald-type ligand, Ruphos. First, the π -complexation to the conjugated system is significantly less for Pd than for Ni.¹¹ Next, Pd in combination with the bulky Ruphos ligand, offers a catalytic system that is extremely stable when free in solution.¹² Finally, high turnover efficiencies, sterically hindered couplings and couplings with electronically different molecules are reported for Ruphos, which should make it applicable for a broad variety of monomers.¹³

Test experiments pointed out that a Negishi coupling was most appropriate for this catalyst. Therefore, we used monobromo-monobromozinc monomers. The electron donating organozinc deactivates the C-Br bond for oxidative addition from Pd[Ruphos]. The monomers are accessible starting from asymmetrically halogenated precursor monomers which undergo a Grignard metathesis (GRIM) followed by a transmetalation with ZnBr₂. The choice for the asymmetric iodine-bromine functionalization is twofold. On one hand this induces selectivity to obtain only one regio-isomer of the monomer and consequently, after polymerization, regioregular polymer. On the other hand, the very reactive iodine functionality, in combination with the appropriate Grignard-reagent, drives the GRIM-reaction to completeness. The latter is needed to provide all the precursor monomers with a deactivating organometallic bond. If not, catalyst transfer to the remaining precursor monomer is possible, which can cause initiation of new chains. The initiator of the polymerization, obtained by the oxidative addition of Pd[Ruphos] to a precursor molecule which only bears a bromine functionality, is prepared and purified in a separate step.

Determining the reaction conditions.

Test experiments were performed in order to determine the most appropriate conditions for Pd-catalyzed coupling reactions. Therefore, 2-bromo-3-hexylthiophene **1a** in dry THF was converted to the Grignard reagent using *i*-PrMgCl.LiCl and transmetalated with ZnBr₂ to the organozinc compound **1b**. Next, 2-halothiophene **2** and finally the catalyst were added. Different (Buchwald)

ligands (DavePhos, SPhos, Ruphos and dppf (dppf = 1,1'-bis(diphenylphosphino)ferrocene)), halogens (Br and I), temperatures and ligand/Pd ratios (1.0 and 1.5) were employed. Only the addition of Pd/Ruphos in a 1/1 ratio to 2-bromothiophene **2** at room temperature delivered the desired end product in a quantitative way and without scrambling (). The high electron density and the steric effects of the bulky Ruphos ligand facilitate the oxidative addition and reductive elimination, respectively. Moreover, again due to these steric effects and a Pd/Ruphos ratio of 1/1, the formation of inactive Pd[Ruphos]₂ is suppressed and only the very reactive, coordinatively unsaturated 12-electron complex Pd[Ruphos] is obtained.^{12,13,14}

Monomer synthesis.

Both thiophene and fluorene derived monomers were employed. The thiophene precursor monomer, 2-bromo-5-iodo-3-hexylthiophene **3a**, is synthesized as described.¹⁵ 2-Bromo-7-iodo-9,9-dioctylfluorene **4a** was synthesized similar to the procedure described for 2-bromo-7-iodo-9,9-dihexylfluorene.¹⁶ Thus, 2-bromofluorene **5** is in a first step iodinated in the 7-position using I₂ and NaIO₃ in a mixture of acetic acid, sulfuric acid and water. Subsequently, this iodinated product **6** is substituted with *n*-octyl chains on the 9-position by reacting *n*-octyl bromide in the presence of NaOH in DMSO with NaI as a catalyst ().

One of the main requirements of the polymerization protocol described above is the complete conversion of precursor monomers **3a** and **4a** via the organomagnesium compounds **3b** and **4b** to the organozinc monomers **3c** and **4c** (). Test experiments were conducted to indicate the appropriate Grignard Metathesis conditions for complete conversion of **3a** and **4a**. While reaction of **3a** with *i*-PrMgCl.LiCl¹⁷ at 40 °C during 20 min appeared to be the proper GRIM-condition for the thiophene precursor monomer, a more reactive turbo-Grignard reagent Bu₂i-PrMgLi at – 40 °C during 45 min is needed for the complete and clean conversion of the fluorene precursor

monomer **4a** to the Grignard equivalent **4b**.¹⁸ Since the exact concentration of the Grignard-reagent must be known – an excess of Grignard-reagent can give rise to a bismetallated species, a chain stopper, while an excess of **3a/4a** results in the presence of transfer reagent – the Grignard-reagents were titrated with salicylaldehyde phenylhydrazone prior to use.¹⁹ In a next step, the organomagnesium compounds **3b** and **4b** are transformed into the organozinc derivatives **3c** and **4c** through a transmetalation with ultra-dry ZnBr₂. In order to verify the quantitative conversion of all reactions in the monomer formation, an aliquot of the reaction mixture was systematically withdrawn and quenched with D₂O. Work up with diethyl ether and ¹H NMR-analysis allow to monitor the GRIM-reaction, the transmetalation with ZnBr₂ and the amount of possibly formed **1a** and **4d**, originating from protonation by humidity.

Synthesis of the initiators.

If the catalytic cycle of the Negishi reaction is investigated into more detail, it is clear that the polymerization can be initiated with an aryl-Pd[Ruphos]-Br species (Scheme 2). These molecules are readily synthesized by reacting Pd₂(dba)₃ (dba = dibenzylideneacetone), Ruphos and the monohalogenated equivalent of the precursor monomer, more in particular 2-bromo-3-hexylthiophene **1a** and 2-iodo-9,9-dioctylfluorene **4f**, in toluene (). Afterwards, the crude mixture is filtered over celite and precipitated in pentane. The initiators are analyzed with ¹H NMR. Interestingly, these Pd-initiators are air-, moisture- and solution-stable molecules, and therefore easy to handle, in contrast to the initiators applied for the Ni-based protocol.

P3HT-homopolymerization.

The homopolymer poly(3-hexylthiophene) (P3HT) was synthesized by adding 1 mol% of the corresponding initiator **3e** in dry THF to the organozinc monomer **3c** at room temperature. During the polymerization, aliquots were withdrawn from the polymerization mixture and quenched with acidified THF. The remaining monomer concentration was determined using gas chromatography

(GC) and gel permeation chromatography (GPC) and the conversion was calculated. As no discrepancy between both techniques were present; the conversions were calculated using the GPC-values. The molar mass of the unfractionated polymers was determined by GPC.

The linear $\ln([M]_0/[M])$ versus time relationship, as shown in A, demonstrates the absence of termination processes. Furthermore, the linear relationship between $\overline{M}_n$ and the conversion, presented in B, clearly show the absence of transfer reactions. Finally, an experiment was performed in which we add 0.5 mmol additional monomer **3c** after the complete consumption (*i. e.* after 1 hour) of the initially loaded 1.5 mmol monomer **3c**. Samples were withdrawn and analyzed with GPC and $^1\text{H-NMR}$, which demonstrated a successful chain extension. As a consequence, it can be concluded that the polymerization of P3HT using the proposed protocol proceeds via a controlled chain-growth mechanism.

PF-homopolymerization.

Next, the homopolymerization of poly(9,9-dioctylfluorene) (PF) was tried using the same conditions as the P3HT homopolymerization. The monomer consumption was monitored by GPC. Again, the linear $\ln([M]_0/[M])$ versus time plot (A) demonstrates the absence of termination reactions, which is in line with the robustness of the catalyst system, being able to promote the Negishi reaction on different systems.

However, when $\overline{M}_n$ versus conversion is plotted, no linear relationship is found (B). Instead, the curve levels off at already low conversions and a steep increase is observed at high conversions. This points at the formation of many new polymer chains at the beginning of the polymerization (transfer reactions) and recombination of those oligomers at the end (step-growth).

Based on an article of Lei and coworkers,²⁰ we hypothesized that a second transmetalation step occurs in case of the poly(fluorene). During this second transmetalation step, a polymer bearing an oxidatively inserted Pd[Ruphos] at the end (**7**) and two monomers (**4c**) are converted into a dibromo functionalized dimer **8** and a polymer chain equipped with an organozincio-functionality (**9**). Due to the lack of a deactivating organometallic bond in compound **8**, the latter becomes active for oxidative addition (on both sides) and a new chain can be initiated. This reaction (A), which results in the formation of new chains, is favored in the beginning of the polymerization when a high monomer concentration is present. In the latter stages of the polymerization, when **9** has accumulated and the monomer concentration has decreased, reaction **B** becomes more important and the amount of polymer chains decreases. This can explain the evolution seen in B.

The ratio of reductive elimination, and the second transmetalation is thus determined by the actual monomer concentration. Indeed, as

$$r_{T.M.II} = k_{T.M.II} \cdot [10] \cdot [4c] \quad (i)$$

$$r_{R.E.} = k_{R.E.} \cdot [10] \quad (ii)$$

$$\frac{r_{R.E.}}{r_{T.M.II}} = \frac{k_{R.E.}}{k_{T.M.II}} \cdot \frac{1}{[4c]} \quad (iii)$$

in which 'R.E.' and 'T.M.II' denote for reductive elimination and second transmetalation, respectively. Therefore, the reductive elimination will be favored if (i) $k_{R.E.} \gg k_{T.M.II}$, which depends on the nature of the actual monomer, and (ii) by a low monomer concentration.

To investigate this hypothesis, we carried out two test experiments. In one reaction, a vessel was loaded with compound **4e** to which 4-bromozincio-anisol **11b** was slowly added (A). In the other reaction, **4e** was slowly added to **11b** (B). When the reactions were completed, the mixtures were

quenched with D₂O, extracted with diethyl ether and both crude products were analyzed with ¹H-NMR spectroscopy. For experiment A, the ¹H NMR-spectrum (Figure S1) demonstrates the absence of compounds **13** and **14** - products formed in the second transmetalation step, while these compounds could clearly be found in experiment B (Figure S2). In summary, these experiments demonstrate that a second transmetalation and the unwanted side reactions related with this are efficiently prevented by keeping the monomer concentration low.

If the unwanted behavior of the PF homopolymerizations is indeed due to the presence of a second transmetalation, it can be suppressed by a continuously low monomer concentration, *i.e.* by slow addition of the monomer during the polymerization. Since the $\overline{M}_n$ versus conversion (p) plot requires that aliquots are withdrawn during the polymerizations, this severely complicates the experiment. Nevertheless,

$$\overline{M}_n = p \cdot \frac{n_{\text{monomer added}}}{n_{\text{initiator added}}} \quad (\text{iv})$$

$$\frac{1}{\overline{M}_n} = \frac{1}{p} \cdot \frac{n_{\text{initiator added}}}{n_{\text{monomer added}}} \quad (\text{v})$$

hold, in which $n_{\text{monomer added}}$ and $n_{\text{initiator added}}$ represent the total amount of monomer and initiator added, respectively. Therefore, we carried out several polymerizations, keeping p constant ($p \approx 1$), but varying $n_{\text{initiator added}}/n_{\text{monomer added}}$. The conversion was verified to be $p \approx 1$ in all cases. The linear relationship (C) demonstrates that no transfer reactions, nor a step-growth mechanism takes place.²¹ Together with the absence of termination processes as shown above, a controlled chain-growth mechanism for the polymerization of poly(9,9-dioctylfluorene) was demonstrated. It must be mentioned that this protocol – the slow addition of monomer – can also be applied on the P3HT polymerization, providing us with a general protocol.

Decomplexation of the catalyst.

As already mentioned, one of the key differences between the existing protocols resulting in controlled polymerizations of CPs and the method presented, is the fact that in the present method the catalyst is continuously released from and reinserted into the growing polymer chains. In order to investigate whether this is indeed the case, we carried out 6 experiments, each time with the same amount of thiophene monomer **3c** and initiator **3e**, but with different amounts of additionally added 2-bromo-3-hexylthiophene **1a**. All the polymerizations were performed with the same conversion ($p \approx 1$) and the molar mass of the polymers was analyzed by GPC. Because of the absence of a deactivating organozinc functionality in **1a**, the C-Br is available for oxidative addition. If the Pd[Ruphos] moiety is released in solution and can reinsert into a non-deactivated C-Br bond, one obtains a linear relation between the inverse of $\overline{M}_n$ and the amount of **1a**. Indeed,

$$\overline{M}_n = p \cdot \frac{n_{3c}}{n_{3e} + n_{1a}} \quad (\text{vi})$$

$$\frac{1}{\overline{M}_n} = \frac{n_{3e}}{p \cdot n_{3c}} + \frac{1}{p \cdot n_{3c}} \cdot n_{1a} \quad (\text{vii})$$

with n_{3e} the amount of initiator added, n_{3c} the total amount of monomer added and n_{1a} the amount of additionally added **1a**. If the catalyst remains complexed with the propagating polymer chains, $1/\overline{M}_n$ is not affected, as is found in the present protocols.^{5g, 6a, 22} clearly shows linearity between $1/\overline{M}_n$ and n_{1a} , at low $(n_{1a} + n_{3e})/n_{3c}$, proving the release and reinsertion of the Pd[Ruphos] moiety during the reaction.

At high amounts of added **1a** ($n_{1a} \gg n_{3e}$), the graph levels off. This indicates that a minimum of monomer additions occur before the Pd is actually released. Extrapolation to infinite n_{1a}/n_{3e} ratio, which corresponds to a condition in which the Pd-catalyst after decomplexation always inserts in

1a and not in a growing polymer chain, results in $1/\overline{M}_n = 6.0 \cdot 10^{-4} \text{ mol/g}$ and $\overline{M}_n = 1.6 \cdot 10^3 \text{ g/mol}$ or $DP \approx 4$ ($DP = \text{degree of polymerization}$). This shows that in the conditions (monomer, temperature etc.) employed, approximately 4 monomer additions occur, after which the catalyst is released. Then, it can either reinsert in a ‘dormant’ polymer chain, a transfer reagent etc. Moreover, this corresponds perfectly to $\overline{M}_n$ at $p \sim 0.1$ B. In this condition the Pd-moiety did not yet dissociate from the polymer molecule and growth has only occurred at the initiator molecules. Since an average of 4 monomers is added, this corresponds to $p = 0.1$ ($4 \times 2.5 \text{ mol\%}$). Such initial polymer molecules have $\overline{M}_n \approx 0.7 \text{ kg/mol}$. Furthermore this also explains the rather high polydispersity. Indeed, one would expect the statistically derived PDI ($PDI \approx 1 + 1/DP$). The latter equation only holds if many ‘propagations-events’ occur. However, if one ‘propagation-event’ accounts for the addition of ± 4 monomers and given that $DP = 15$, only 4 ‘extension events’ occur. Consequently, the statistically derived equation does not hold.

From the above findings, it is clear that care must be taken to work under ultra dry circumstances. Indeed, if the organozincio-bond is quenched, due to humidity, during the monomer preparation or the polymerization, the monomers **3c** and **4c** are converted to **1a** and **4d** respectively, which are able to initiate new polymer chains, and therefore destroy the controlled character of the chain-growth mechanism.

Block-copolymers.

Finally, block-copolymer composed of a poly(3-hexylthiophene) and a poly(9,9-dioctylfluorene) block are prepared by successive addition of the monomers, starting from **3e** or **4e** (2.5 mol%), depending on the nature of the first block. Samples were taken after the first block and systematically during the polymerization of the second block and subsequently analyzed with

GPC. A systematic increase of $\overline{M}_n$ during the polymerization of the second block demonstrates the chain-growth nature of the used protocol (Figure S3 & S4). shows a clear shift of the final block-copolymer to higher molar masses and a unimodal shape, which proves the successful elongation of the first block. The $\overline{M}_n$ and PDI values of the first block and the final block-copolymers, as determined by GPC, are listed in . The PDI decreases upon the block-copolymer formation, as expected since the number of chain extension events increases. ^1H NMR and UV-vis spectra confirmed presence of both blocks (Figure S5, S16, S17).

It is remarkable that the synthesis of the block-copolymers can be done in both directions - the polymerization sequence is of no matter. This behavior is unobserved in the existing polymerization protocols and makes the presented Pd[Ruphos]-protocol unique. Both the groups of Yokozawa and Wang reported the impossibility to polymerize diblock-copolymers in both directions if both blocks are electronically different.^{5f, 23} Kiri attributed this to the energy profile related with the ring walking process of the Ni-moiety.⁸ In the existing protocols a successful synthesis of conjugated block-copolymers is only possible if the second block shows a higher affinity for the catalyst moiety than the previous block. If not, the catalyst will remain at the block with the highest affinity, *i.e.* the first, and therefore it cannot reach the polymer end to propagate. In the presented protocol an additional pathway is provided, *i.e.* through the solution after decomplexation from the polymer chain (). This demonstrates the universal nature of the protocol and becomes extremely useful in the synthesis of tri- or higher-block-copolymers. Indeed, if, for instance, a tri-block-copolymer A-B-C can be formed using the existing protocols, the A-C-B triblock-copolymers cannot. Even more, block-copolymers of tailor-made electron rich and electron poor monomers, are coming within reach.

General relevance.

It must be mentioned that the fact whether or not the catalyst has a strong tendency to remain complexed with the π -system of a compound, is not only important for the polymerization of CPs, but it is also relevant in the synthesis of small molecules. More in particular, it determines whether and to which extent reaction with one equivalent of an organometallic compound together with a dihalogenated aryl compound results in mono-reacted or in di-reacted product. Indeed, a catalytic system with a strong tendency for complexation with the π -system remains associated with the mono-reacted compound and a second oxidative addition readily occurs, resulting in di-reacted product. In other systems, the catalyst diffuses away after the catalytic cycle and mono-reacted products are also found. The outcome of the reaction therefore depends on the efficiency of the diffusion process in competition with the second oxidative addition. It appears that the ligand of the Pd-catalyst, and to a limited extent also the nature of the halogen, is decisive in this respect.²⁴ Di-reaction is typically found in the condition in which a controlled polymerization was obtained using Suzuki reactions, *i. e.* in the presence of Pd[PtBu₃]. The formation of mono-substituted aryl compounds therefore requires conditions in which the catalyst is easily released from the polymer chains. Indeed, 2-dicyclohexylphosphino-biphenyl, a Ruphos-like ligand, delivers a major fraction of mono-reacted product in the Suzuki cross-coupling, indicating a liberated Pd[ligand] moiety.^{24b} As a consequence, it is clear that these two fields (development of a protocol for the controlled polymerization of CPs and mono- versus di-reaction in dihalogenated aromatic compounds) are complementary.

Experimental

Reagents and instrumentation.

All reagents were purchased from Aldrich Chemical Co., Acros Organics and Alfa Aesar. Reagent grade solvents were dried and purified by distillation. Tetrahydrofuran (THF) and toluene were dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina). Gel permeation chromatography (GPC) measurements were performed with a Shimadzu 10A apparatus with a tunable absorbance detector and a differential refractometer in THF as eluent toward polystyrene standards. ^1H nuclear magnetic resonance (^1H NMR) measurements were carried out with a Bruker Avance 300, 400 or 600 MHz. UV-vis spectra were recorded with a Varian Cary 400 apparatus. Compound **1a**,⁴ **3a**,⁴ **3b**,⁴ **3c**,⁴ **6**¹⁵ and **4d**¹⁵ are synthesized as described in the literature.

7-Bromo-2-iodo-9,9-dioctylfluorene (4a).

Compound **6** (38.8 mmol, 14.4 g), 1-bromooctane (97.7 mmol, 17.0 mL) and NaI (1.33 mmol, 0.200 g) were dissolved in dry DMSO (220 mL) and kept under argon. Finely grained sodium hydroxide (137 mmol, 5.50 g) was added and the reaction was monitored with TLC. When the reaction had finished, the mixture was poured in ice water and extracted with hexane. The organic layer was washed with a saturated NaHCO_3 -solution and subsequently with brine. After drying with MgSO_4 and concentration, the residual 1-bromooctane was removed under reduced pressure (50 °C, 1 mmHg) and the crude product was purified by column chromatography (silica, eluent: petroleum ether 40/60) resulting in a white solid. Yield: 17.4 g (75%). mp: 42.0 °C. ^1H NMR (CDCl_3): δ = 7.65 (d, J = 7.60 Hz, 1H), 7.64 (s, 1H), 7.52 (d, J = 7.50 Hz, 1H), 7.45 (d, J = 7.50 Hz, 1H), 7.43 (s, 1H), 7.40 (d, J = 7.60 Hz, 1H), 1.90 (qu, 4H), 1.15 (m, 20H), 0.83 (t, 6H), 0.57 (t, 4H). ^{13}C NMR (CDCl_3): δ (ppm) = 153.1, 152.7, 140.0, 139.5, 136.4, 132.4, 130.5, 126.5, 122.0, 121.8, 121.5, 93.3, 56.0, 40.45, 32.1, 30.2, 29.5, 29.4, 24.0, 23.0, 14.4.

2-Iodo-9,9-dioctylfluorene (4f).

The bromide **4d** (5.32 mmol, 2.50g) was brought under argon atmosphere and dissolved in dry THF (60.0 mL). When the solution was cooled to - 78 °C, *n*-BuLi was added (5.59 mmol, 2.24 ml). After 20 min of stirring at - 78 °C, I₂ (15.0 mmol, 3.81g), dissolved in dry THF (30.0 mL), was cannulated . After 30 min, the reaction mixture was allowed to reach room temperature and a saturated Na₂S₂O₃-solution was added. Next, the mixture was extracted with hexane, the organic layer was washed with a saturated NaHCO₃-oplossing and brine and finally dried with MgSO₄. After solvent removal under reduced pressure, column chromatography (silica, eluent: petroleum ether 40/60) delivered the desired colorless oil. Yield: 1.05 g (38%). ¹H NMR (CDCl₃): δ = 7.61 – 7.69 (m, 3H), 7.43 (d, J = 6.70 Hz, 1H), 7.35 – 7.29 (m, 3H), 1.91 (qu, 4H), 1.35 – 0.95 (m, 20H), 0.82 (t, 6H), 0.59 (t, 4H). ¹³C NMR (CDCl₃): δ (ppm) = 153.5, 150.4, 141.1, 140.5, 136.2, 132.4, 128.0, 127.2, 123.1, 121.7, 120.1, 92.9, 55.6, 40.8, 32.2, 30.4, 30.1, 29.6, 24.0, 23.0, 14.5.

Initiator 3e.

2-Bromo-3-hexylthiophene **1a** (4.00 mmol, 0.989 g) was dissolved in dry toluene (10.0 mL) under argon atmosphere and Pd₂(dba)₃ (1.00 mmol, 0.916 g) and Ruphos (2.03 mmol, 0.945 g) were added. Next, the reaction mixture was purged with argon and subsequently heated to 60 °C. After 3 hours, most of the solvent was evaporated under reduced pressure and the crude product was dissolved in diethyl ether (25.0 mL). The mixture was filtered over celite, concentrated and precipitated in pentane (50.0 mL). After 2 hours of stirring at 5 °C, the precipitate (dba) was filtered. The filtrate was concentrated again, dissolved in pentane (20.0 mL) and stirred overnight for precipitation at 5 °C. The pure initiator was obtained after filtration as a yellow solid. Yield: 611 mg (37%). mp: 180 °C (decomposes). ¹H NMR (CDCl₃): δ = 7.68 (m, 1H), 7.60 (m, 1H), 7.30 – 7.50 (m, 2H), 7.28 (d, J = 4.00 Hz, 1H), 6.83 (m, 2H), 6.65 (d, J = 7.70 Hz, 1H), 6.59 (d, J = 7.60 Hz, 1H), 4.58 (m, 2H), 2.81 (m, 1H), 2.62 (m, 2H), 2.34 (m, 1H), 2.21 (m, 1H), 1.90 – 0.80 (m, 41 H), 0.70 (m, 1H). ¹³C NMR (CDCl₃): δ (ppm) = 170.0, 160.1, 145.2, 145.0, 136.3, 134.7, 134.2, 126.9, 126.3, 114.1, 114.0, 109.0, 108.9, 107.3, 107.1, 71.6, 70.5, 35.3, 35.4, 35.0,

34.1, 33.7, 32.0, 30.2, 30.1, 29.9, 28.6, 27.8, 27.7, 27.3, 27.2, 27.0, 26.9, 26.8, 26.1, 25.9, 25.6, 22.9, 22.6, 22.4, 22.1, 21.7, 21.6, 14.3.

Initiator 4e.

The same procedure as described for initiator **3e** was used, starting from **4f** (2.03 mmol, 1.05 g) in dry toluene (60.0 ml), Pd₂(dba)₃ (0.850 mmol, 0.778 g) and Ruphos (1.70 mmol, 0.793 g). A yellow solid was obtained. Yield: 1.15 g (43%). mp: 130 °C. ¹H NMR (CDCl₃): δ = 7.75 (d, J = 15.8 Hz, 2H), 7.70 – 7.57 (m, 7H), 7.54 (d, J = 7.40 Hz, 1H), 7.50 – 7.30 (m, 8H), 7.30 – 7.15 (m, 3H), 7.10 (d, J = 15.8 Hz, 2H), 7.08 (m, 1H), 6.99 (s, 1H), 6.87 (m, 1H), 6.73 (d, J = 8.5 Hz, 1H), 6.68 (d, J = 8.5 Hz, 1H), 4.62 (m, 2H), 2.40 – 0.50 (m, 68H). ¹³C NMR (CDCl₃): δ (ppm) = 188.9, 158.8, 158.5, 149.6, 149.1, 144.6, 143.3, 142.0, 136.5, 134.8, 134.3, 133.3, 132.8, 132.7, 130.9, 130.5, 130.2, 129.0, 128.4, 126.2, 125.7, 125.4, 122.6, 118.8, 117.0, 112.4, 108.3, 107.7, 71.2, 70.6, 54.5, 40.9, 40.5, 31.8, 31.7, 30.6, 30.2, 29.6, 29.3, 28.4, 27.7, 27.0, 26.7, 26.2, 25.8, 24.1, 23.5, 22.6, 22.3, 22.2, 21.8, 21.3, 14.1, 14.0.

Turbo Grignard-reagent Bu₂*i*-PrMgLi and titration.

Dry THF (5 mL) was cooled to 0 °C and kept under argon atmosphere. A solution of *i*-PrMgCl.LiCl (3.13 mmol, 2.40 ml) in THF and *n*-BuLi (6.25 mmol, 2.50 mL) in hexane are added respectively and the mixture was stirred for 1 h at 0 °C. After 1 h, three titrations with salicylaldehyde phenylhydrazone were conducted under argon atmosphere. The average of the three outcomes was used as the concentration of the magnesium-ate turbo Grignard-reagent.

Synthesis of monomer 3c.

The precursor monomers **3a** (1.05 mmol, 0.391 g) was loaded in a flask, dissolved in dry THF (5 ml) and purged with argon. In a next step, the solution was heated to 40 °C and an equimolar amount of *i*-PrMgCl.LiCl in THF (1.05 mmol, 0.860 ml) was added. A sample (0.025 mmol) was

withdrawn from the reaction mixture after 20 min stirring at 40 °C and quenched with D₂O, extracted with diethyl ether and concentrated in order to evaluate the quantitative and selective conversion to **3b** with ¹H NMR spectroscopy. In a next step, the organomagnesium product was cannulated to a flask loaded with ultra-dry ZnBr₂ (2 mmol, 0.45 g) at room temperature and subsequently rinsed with dry THF (1 mL). After 30 min of stirring, an aliquot (25.0 μmol) was withdrawn from the reaction mixture and poured into D₂O and analyzed with ¹H NMR spectroscopy to verify the purity of the monomer.

Synthesis of monomer 4c.

The precursor monomers **4a** (1.05 mmol, 0.625 g) was loaded in a flask, dissolved in dry THF (5 ml) and purged with argon. Subsequently, the solution was cooled to - 40 °C and an equimolar amount of Bu₂*i*-PrMgLi in hexane (1.05 mmol, 1.15 mL) was added. A sample (0.025 mmol) was withdrawn from the reaction mixture after 45 min stirring at - 40 °C and quenched with D₂O, extracted with diethyl ether and concentrated in order to evaluate the quantitative and selective conversion to **4b** with ¹H NMR spectroscopy. In a next step, the organomagnesium product was cannulated to a flask loaded with ultra-dry ZnBr₂ (2 mmol, 0.45 g) at 0 °C and subsequently rinsed with dry THF (1 mL). After 30 min of stirring, an aliquot (25.0 μmol) was withdrawn from the reaction mixture and poured into D₂O and analyzed with ¹H NMR spectroscopy to verify the purity of the monomer.

Poly(3-hexylthiophene) (P3HT).

The organozinc monomer **3c** (1.05 mmol, c = 0.125 M in THF) was prepared as described in the general procedure above. 1 Mol% initiator **3e** (10.0 μmol, 8.20 mg), dissolved in dry THF (1 mL), was added to the monomer **3c** (1.00 mmol) and the reaction mixture was kept at room temperature. Samples were withdrawn during 60 min with a syringe and quenched in acidified THF. The samples were analyzed with GPC to evaluate the monomer conversion and the molar

mass of the polymers. After 60 min, the polymerization was quenched with acidified THF and the polymer was precipitated in methanol, filtered off and dried. ^1H NMR (CDCl_3): δ = 7.16 (d, 0.08H), 7.02 – 6.94 (m, 1H), 6.53 (d, 0.08H), 2.80 (t, br, 1.6H), 2.56 (t, br, 0.5H), 1.69 (s, br, 2.1H), 1.45 – 1.30 (m, 7H), 0.91 (t, br, 3.3H).

Poly(9,9-dioctylfluorene) (PF).

The organozinc monomer **4c** (1.05 mmol, c = 0.125 M in THF), prepared as described in the general procedure above, was slowly added to a solution of 2.5 mol% initiator **4e** (25.0 μmol , 33.0 mg) in dry THF (1 mL) and the polymerization mixture was kept at room temperature during 1 hour. Samples were withdrawn during 60 min with a syringe and quenched in acidified THF. The samples were injected in GPC to evaluate the monomer conversion and the molar mass of the polymers. After 60 min, the polymerization was quenched with acidified THF and the polymer was precipitated in methanol, filtered off and dried. ^1H NMR (CDCl_3): δ = 7.75 – 7.73 (m, 1.5H), 7.68 – 7.61 (m, 4.1H), 7.52 – 7.49 (m, 0.1H), 7.36 – 7.32 (m, 0.4H), 7.17 (s, br, 0.3H), 2.2 – 1.9 (m, br, 4H), 1.3 – 1.0 (m, 21.8H), 0.9 – 0.6 (m, br, 10.7H).

Poly(3-hexylthiophene)-*b*-poly(9,9-dioctylfluorene) (P3HT-*b*-PF).

The organozinc monomers **3c** (1.05 mmol) and **4c** (1.05 mmol) were synthesized using the method described above. The polymerization was initiated by adding **3c** to a solution of 4 mol% **3e** (40.0 μmol , 32.8 mg) in dry THF (1 mL) over 5 min and the mixture was kept at room temperature. Aliquots were withdrawn from the polymerization mixture after 20 min (0.300 mL) and 45 min (0.800 mL) and quenched in acidified THF. After 45 min, the next monomer **4c** was added in a timespan of 10 min and aliquots were withdrawn and quenched in acidified THF during 60 min for GPC analysis. After overnight stirring, the polymerization mixture was quenched with acidified THF and the polymer was precipitated in methanol, filtered off and dried. m = 25.8 mg (14%) ^1H NMR (CDCl_3): δ = 7.78 – 7.73 (m, 1.1H), 7.71 – 7.62 (m, 3.1H),

7.52 – 7.49 (m, 0.1H), 7.37 – 7.32 (m, 0.4H), 7.17 (s, br, 0.3H), 7.05 – 6.94 (m, 1H), 2.81 (t, br, 1.3H), 2.56 (t, br, 0.7H), 2.2 – 1.9 (m, br, 3.1H), 1.8 – 1.5 (m, 2.7H), 1.45 – 1.0 (m, 24.0H), 0.9 – 0.6 (m, br, 12.0H).

Poly(9,9-dioctylfluorene)-*b*-poly(3-hexylthiophene) (PF-*b*-P3HT).

The organozinc monomers **3c** (1.05 mmol) and **4c** (1.05 mmol) were synthesized using the method described above. The polymerization was initiated by adding **4c** to a solution of 4 mol% **4e** (40.0 μ mol, 53.0 mg) in dry THF (1.00 mL) over 5 min and the mixture was kept at room temperature. Aliquots were withdrawn from the polymerization mixture after 20 min (0.300 mL) and 45 min (0.800 mL) and quenched in acidified THF. After 45 min, the next monomer **3c** was added in a time span of 5 min and aliquots were withdrawn and quenched in acidified THF during 60 min for GPC analysis. After stirring overnight, the polymerization mixture was quenched with acidified THF and the polymer was precipitated in methanol, filtered off and dried. m = 39.9 mg (10 %) ^1H NMR (CDCl_3): δ = 7.73 – 7.68 (m, 1.4H), 7.65 – 7.61 (m, 3.8H), 7.52 – 7.49 (m, 0.2H), 7.37 – 7.32 (m, 0.4H), 7.17 (s, br, 0.3H), 6.98 – 6.93 (m, 0.8H), 2.81 (t, br, 1.3H), 2.56 (t, br, 0.4H), 2.2 – 1.9 (m, br, 4.0H), 1.8 – 1.5 (m, 2.4H), 1.45 – 1.0 (m, 26.5H), 0.9 – 0.6 (m, br, 13.4H).

Conclusion

In conclusion, we present a universal chain-growth polymerization protocol for conjugated polymers of which the controlled nature does not rely on system-specific interactions. We demonstrated that the stable Pd[Ruphos] catalyst is easily released from the propagating polymer chain to the solution, and readily re-inserts into a “dormant” polymer chain. This provides the opportunity to synthesize block-copolymers in a one-pot synthesis by successive monomer addition. A chain-growth mechanism is demonstrated for P3HT and PF. Block-copolymers P3HT-*b*-PF and PF-*b*-P3HT are successfully synthesized using this protocol and the sequence for

this synthesis is unimportant, which can be attributed to the system-independent, and therefore universal, nature of the presented Pd[Ruphos] protocol. This broadens the synthetical scope for tailor-made conjugated polymers. Further research will focus on the controlled polymerization of many other CPs and their block-copolymers.

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Supplementary Information

¹H NMR spectra of the crude products from the reactions shown in A and B, GPC chromatograms of the block-copolymer formation, UV vis and ¹H NMR spectra of the homopolymers and the block-copolymers are provided. This material is available free of charge via the Internet at <http://onlinelibrary.wiley.com>.

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polymerization of P3ATs does not originate from this principle, but from the fact that the catalyst is not released from the polymer chains.

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(21) If the polymerization proceeds via a chain-growth mechanism and $p \approx 1$, $1/\overline{M}_n \sim n_{\text{initiator}}$

added/ $n_{\text{monomer added}}$; If the polymerization proceeds via a step-growth mechanism and $p \approx 1$, $1/\overline{M}_n \sim$

$n_{\text{initiator added}}/(n_{\text{monomer added}} + n_{\text{initiator added}})$, which deviates from the above-mentioned equation for non-negligible $n_{\text{initiator added}}$.

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Caption to Figures and schemes

Scheme 1. Monomer design used by Yokozawa for a polyamide formation in a chain-growth fashion.

Scheme 2. Schematic representation of the existing and presented polymerization protocols.

Control in the present protocols is realized by suppressing path A; control in the proposed protocol is obtained by suppressing path B and favoring path D.

Scheme 3 Test reactions to determine the optimal conditions for polymerization and the obtained products.

Scheme 4. Synthesis of compound **4a**.

Scheme 5. Synthesis of the thiophene monomer **3c** and the fluorene monomer **4c** using a GRIM-reaction and a transmetallation.

Scheme 6 Synthesis of the initiators **3e** and **4e**.

Scheme 7. Up: Catalytic cycle showing the competition between reductive elimination (R.E.) and a second transmetallation (T.M.II) (O.A. = oxidative addition); Down: (A) Formation of a bifunctional initiator **8** resulting from the second transmetallation; (B) Recombination of two polymer chains.

Scheme 8. Influence of the order of addition on the ratio of the second transmetallation and reductive elimination.

Figure 1. (A) $\ln([M]_0/[M])$ versus time for P3AT; (B) $\overline{M_n}$ versus conversion. The experiments were conducted in THF at room temperature with $[M]_0 = 0.16$ M; $[In]_0 = 3.2$ mM.

Figure 2. (A) $\ln([M]_0/[M])$ versus time for PF. At the last data point, all monomer had been consumed, which explains the slight deviation. (B) $\overline{M_n}$ versus conversion at fast monomer addition and (C) $1/\overline{M_n}$ versus the amount of initiator added divided by the total amount of monomer added at slow monomer addition; the conversion equals 0.98-1 in all these experiments.

All experiments were conducted in THF at room temperature with $[M]_0 = 0.13$ M and $[In]_0 = 3.2$ mM for (A) and (B); $n_{\text{monomer added}} = 0.675$ mmol for (C).

Figure 3. Relationship between the $1/\overline{M}_n$ and the amount of additionally added **1a**. The

experiments were conducted in THF at room temperature. $n_{3e} = 0.01$ mmol, $n_{3c} = 1$ mmol.

Figure 4 (A) GPC chromatograms of the block-copolymer formation of P3HT-*b*-PF starting from the thiophene-block; (B) the block-copolymer formation of PF-*b*-P3HT starting from the fluorene-block.

Graphical Abstract

In this manuscript, a new approach is presented to achieve a universal chain growth polymerization protocol for conjugated polymers. The protocol is applied on the polymerization of the homopolymers poly(3-alkylthiophene) and poly(9,9-dioctylfluorene) and block-copolymers of them. During the synthesis of the latter, the sequence of monomer addition seemed to be unimportant, which denotes the universal character of the presented protocol.