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Influence of Alkyl Substitution Pattern on Reactivity of Thiophene-Based Monomers in Kumada Catalyst-Transfer Polycondensation

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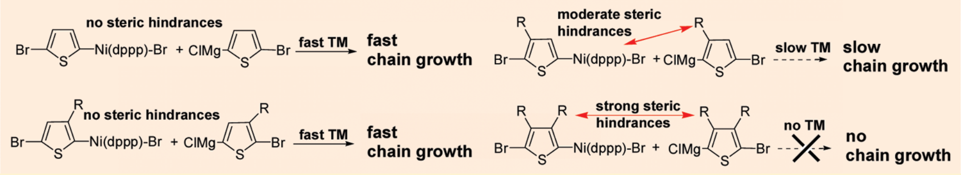
Supporting Information

ABSTRACT:



Transmetalation (TM) was found to be the key step defining the ability of alkyl-substituted thiophene-based ClMg-Th(R)-Br monomers to be polymerized under Ni-catalyzed Grignard metathesis/Kumada catalyst transfer polycondensation conditions. For both dppe- and dppp-supported catalysts (dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,2-bis(diphenylphosphino)-propane), chain propagation is prohibited if the TM step would lead to sterically hindered head-to-head (HH) Th(R)-Ni-(R)Th intermediates in which alkyl substituents at both thienyl rings are in the "*ortho*" position relative to the Ni center. However, polymerization proceeds if no alkyl substituents are present at least at one "*ortho*" position relative to the Ni center. This rule is fulfilled for "regular" 2-bromo-5-chloromagnesio-3-hexylthiophene (**2**) which easily polymerize in the presence of various Ni initiators. However, "reversed" 5-bromo-2-chloromagnesio-3-hexylthiophene (**1**) has sterically hindered Grignard function and therefore the initiation step is hampered with Ni(dppe)Cl_2 or Ni(dppp)Cl_2 initiator precursors, but it proceeds with sterically nonhindered Ph-Ni(dppe)-Br and Ph-Ni(dppp)-Br initiators. "Disubstituted" 2-bromo-5-chloromagnesio-3,4-dihexylthiophene (**3**) does not polymerize by any initiators. "Unsubstituted" monomer 2-bromo-5-chloromagnesiothiophene (**4**) smoothly homopolymerizes and copolymerizes with 2-bromo-5-chloromagnesio-3-dodecylthiophene (**2a**) by various unsupported and surface-immobilized initiators via the chain-growth mechanism. This reflects the unimportance of the "*ortho*" stabilization of the chain-propagating Ni species for achieving a good polymerization control, if Ni catalysts are ligated by bidentante dppp and dppe ligands. The obtained results demonstrate that unsubstituted thiophene is a suitable building block for designing of new conjugated polymers via chain-growth Kumada catalyst-transfer polycondensation.

1. INTRODUCTION

Ni-catalyzed chain-growth Kumada catalyst-transfer polycondensation (KCTP)[1−24] of AB-type monomers is an important tool in preparation of well-defined thiophene-,[4,17] fluorene-,[10] phenylene-,[10] and pyrrole-based conjugated homopolymers,[1−4] block copolymers,[7−12] gradient copolymers,[13] and polymer brushes.[14−18] It is believed that such materials have a greater potential for various optoelectronic applications than conventional conjugated polymers available by step-growth polycondensations.[19] Efficient engineering of materials with tailored optoelectronic properties requires involvement into KCTP of new types of monomers, including monomers containing several aromatic rings and monomers with a variable substitution pattern. In many cases polymerization of such monomers involves the chain-growth propagation as a dominating pathway; however, polymerization rates and chain-growth performances vary in a large range. Electronic effects, steric hindrances, and monomer length are possible factors that may contribute to the monomer reactivity and the chain-growth performance. Some attempts to elucidate the influence of substituents on monomer reactivity were undertaken; however, the situation remains uncertain even in the case of the most studied thiophene-based monomers. At the same time, the thiophene unit is an important fragment in various promising monomers, e.g., cyclopenta[2,1-*b*:3,4-*b*]-dithiophenes,[25] dithienosiloles,[26a] dithieno[3,2-*b*:2′,3′-*d*]pyrroles,[26b] thieno(3,4-*b*)thiophenes,[26c] thieno[3,4-*c*]pyrroles-4,6,[27a,b] cyclopenta[1,2-*d*:4,3-*d*′]dithiazoles,[27c] etc., and it is a building block in many useful thiophene-based alternate donor−acceptor copolymers.[28] In most cases, these polymers were synthesized by means of poorly controllable (in terms of molecular weight distribution and end-group functionality) Suzuki, Stille, Yamamoto, or Sonogashira step-growth polycondensations. It is therefore a highly desirable task to develop a general procedure for polymerization of such monomers in

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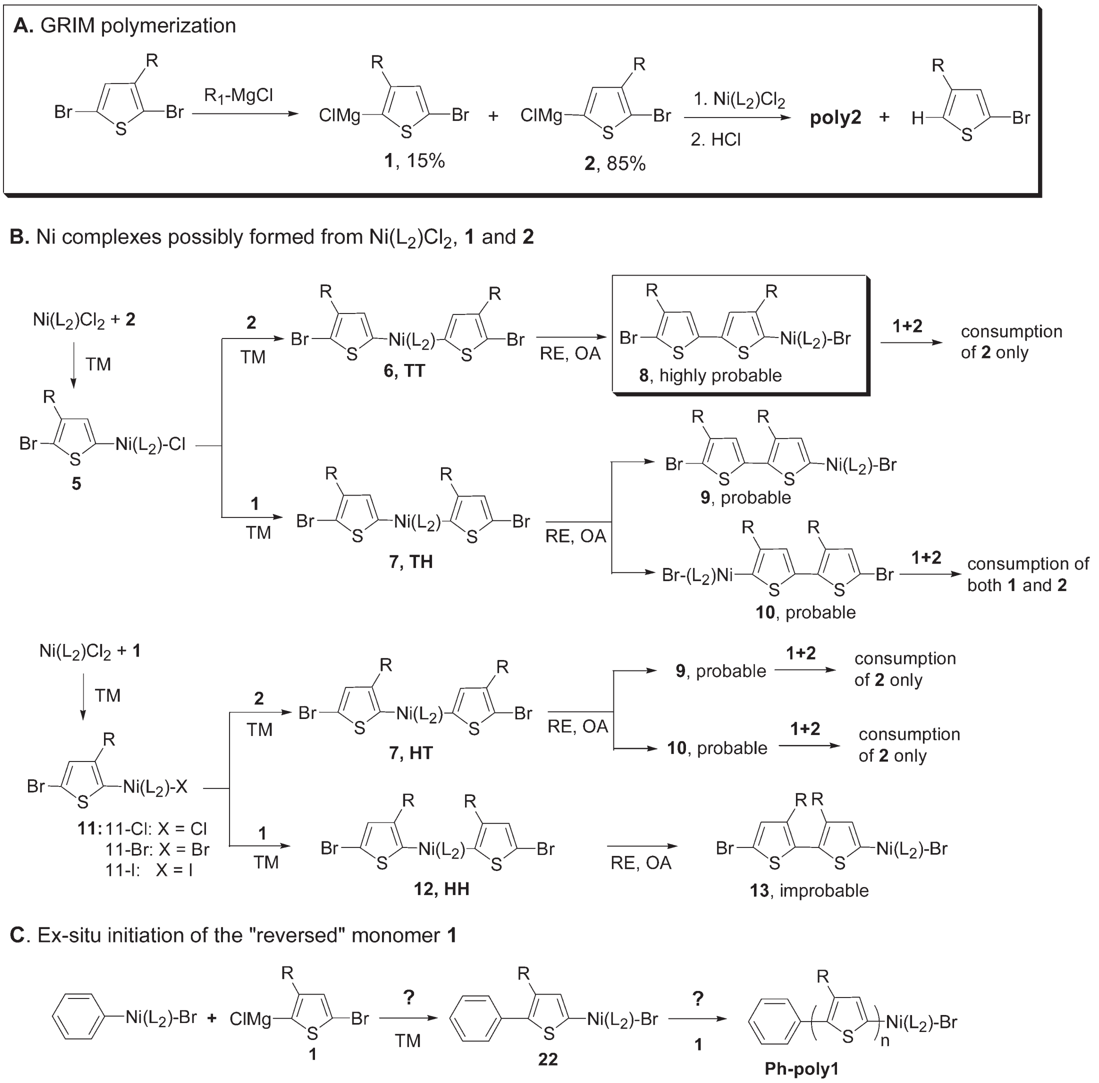
Scheme 1. (A) GRIM Polymerization of Isomeric 5-Bromo-2-chloromagnesio-3-hexylthiophene (1, R = Hex) and 2-Bromo-5-chloromagnesio-3-hexylthiophene (2, R = Hex) into Regioregular HT P3HT Proceeds via Selective Consumption of 2;[1,2] (B) Structure of Ni Complexes Possibly Formed from Monomers 1, 2, and NiL_2Cl_2 That May Act as Initiators in GRIM Polymerization; (C) Initiation of 2 by Sterically Nonhindered Ph-Ni(L_2)-Br



a more controllable way, such as via chain-growth KCTP. However, without a clear understanding of structure—reactivity relationships the polymerization of new monomers will require a tedious trial-and-error development of unique polymerization protocols, and hence, the formulation of general "design rules" for the selection of easy polymerizable monomers is strongly desirable.

Under usual conditions KCTP is initiated by 1 equiv of NiL_2Cl_2 (L_2 = dppe or dppp, dppe = 1,2-bis(diphenylphosphino)ethane, dppp = 1,3-bis(diphenyl phosphino)propane) and 2 equiv of AB-type monomer molecules having Grignard and halogen groups in their structure.[1,2] Alternatively, KCTP can be initiated by externally added Ar-Ni(PPh_3)$_2$-Br,[14] Ar-Ni(dppe)-Br, and Ar-Ni(dppp)-Br[16,21] initiators or by surface-bound initiators.[14−18] Whatever the initiation methods, a chain-propagation catalytic cycle involves transmetalation (TM), reductive elimination (RE), and oxidative addition (OA) as elementary steps. Chain propagation occurs via one-by-one successive addition of monomer molecules to propagating Ni complex. The chain-growth mechanism is provided by the fact that the Ni(0) catalytic species eliminated upon the RE step do not dissociate from the growing chains, but instead form complexes with them and undergo intramolecular OA into the C—Br bond present in the same chains.[1,2]

It is known for years that Grignard metathesis (GRIM) of 2,5-dibromo-3-hexylthiophene and alkylmagnesium chlorides usually leads to a ∼15/85 mixture of isomeric 5-bromo-2-chloromagnesio-3-hexylthiophene (**1**) and 2-bromo-5-chloromagnesio-3-hexylthiophene (**2**), copolymerization of which gives a surprisingly highly regioregular head-to-tail (HT) poly(3-hexylthiophene) (P3HT).[29] It is believed that the regioregularity is provided by the fact that only isomer **2** is reactive, whereas **1** remains intact and gives the protonated product 5-bromo-3-hexylthiophene after acidification (Scheme 1A).

These results led researchers to believe that monomer **1** is completely inert under KCTP (or GRIM polymerization) conditions. As such, the monomer **2** exemplifies itself structural features of a "correctly designed" but **1** of a "wrongly designed" monomer. It is clear that the difference in reactivity is due to the different position of the alkyl substituent; however, it was uncertain what exactly makes the isomer **1** to be unreactive under GRIM polymerization conditions: (1) the absence of the alkyl substituent "*ortho*" to bromine atom or (2) the presence of the alkyl substituent "*ortho*" to the Grignard function. McCullough et al. proposed in their early work to explain the high degree of HT regioregularity of P3HT by a combination of kinetic and thermodynamic effects arising from steric and electronic effects occurring in the catalytic reaction; however, no correct understanding of the polymerization process, such as that it involves the chain-growth catalyst transfer mechanism, existed at that moment.[29] Luscombe et al. investigated polymerization of the "reverse" monomer **1** in the presence of externally added Ph-Ni(dppp)-Cl initiator and proposed that the inability of **1** to polymerize is due to the lack of "*ortho*" stabilization in the propagating Ni complex preventing oxidative addition of the nickel into the Ar—Br bond.[30] We instead propose that transmetalation is the key step defining the ability of alkyl-substituted thiophene-based ClMg-Th(R)-Br monomers to be polymerized under Ni-catalyzed KCTP. We suggest that the initiation and/or chain propagation are prohibited if the TM step leads to sterically hindered head-to-head (HH) Th(R)-Ni-(R)Th intermediates in which alkyl substituents at both thienyl rings are in the "*ortho*" position relative to the Ni center. To verify this hypothesis, reactivity of **1**, **2**, and related 2-bromo-5-chloromagnesio-3,4-dihexylthiophene (**3**) as well as 2-bromo-5-chloromagnesio-thiophene (**4**) monomers was comprehensively investigated. Compound **3** having alkyl substituents at both magnesium and bromine ends was chosen as a model monomer since it combines both structural features of **1** and **2** monomers. On the other hand, monomer **4** has no alkyl substituents neither at the magnesium nor at the bromine ends. Thus, with the monomers **1**−**4** in hands the influence of the substitution pattern onto the GRIM/KCTP can be assessed.

2. RESULTS AND DISCUSSION

2.1. Initiation of GRIM Polymerization. Initiators for GRIM polymerization are formed via two-step transmetalation involving 1 equiv of NiL_2Cl_2 and 2 equiv of monomers. Since there are two isomeric monomers in the mixture, four isomeric intermediates (**8**−**10** and **13**) could, in principle, be formed, as depicted in Scheme 1B. Monomer **2** is present in an excess, and it is less sterically hindered at its magnesium end; thus, **2** may preferentially be involved into the first TM step leading to **5**. By the same reasons, the second TM step should also preferentially proceed with **2** leading to **6** via sterically less demanding transition state in which two monomer residues are attached to Ni center on a tail-to-tail (TT) manner. On the other hand, formation of some amounts of isomeric **11** from **1** and NiL_2Cl_2 at the first TM step cannot be *a priori* excluded. Similarly, monomer **1** may also participate in the second TM reaction leading to complexes in which either one (in **7**) or two (in **12**) alkyl substituents are oriented toward the Ni center. A transition state preceding the intermediate **12**, in which monomer residues are attached in a HH manner, is the most sterically hindered in the series so that the formation of **12** and hence of **13** is improbable here. Formation of **7** from **11** and **2** is probable since monomer residues in this intermediate are HT-linked, i.e., exactly the same way as in regioregular P3ATs upon "quasi-living" GRIM polymerization of the "regular" monomer **2**. It is also noteworthy that the same TH or HT intermediate **7** should be formed from NiL_2Cl_2 and monomers **1** and **2** via different transition states: in one case, the monomer **1** approaches by its sterically hindered magnesium end to the sterically nonhindered Ni center in **5**, whereas in another case, sterically nonhindered monomer **2** attacks the sterically hindered Ni center of **11**. It is *a priori* unclear whether this difference accounts to a different polymerization behavior of **1** and **2**, and this issue will be elucidated in the present work. Reductive elimination followed by intramolecular oxidative addition convert intermediates **6** and **7** into initiators **8**−**10**. Assuming that polymerization would be possible if it proceeds via HT-linked intermediates (like **7**), or sterically even lesser hindered TT intermediates (like **6**), it is expected that polymerization of monomer **2** can be efficiently initiated by any initiators **8**−**10** (Scheme S1, Supporting Information).

Initiators **8**, **10**, and structurally similar species **16** (Scheme S1, Supporting Information) formed upon homopolymerization of **2**, all have sterically hindered Ni centers, and thus they should selectively react only with monomer **2** which has no alkyl substituents *ortho* to the magnesium end to give products **16**−**18**. In contrast, monomer **1** may react only with **9**, and polymerization should continue until the first molecule of **2** adds to the propagating chain end **21** (Scheme S1, Supporting Information). When it happens, further polymerization of **1** should not be possible because it should now involve HH intermediates; however, polymerization of **2** may proceed from those chains.[31] Thus, polymerization of **1** should not be possible if substantial amounts of **2** are present in the mixture. However, the question arises whether polymerization of **1** would proceed in the absence of **2** and, if yes, what initiator should be used? The considerations from Scheme 1 and Supporting Information show that initiation of polymerization of **1** by NiL_2Cl_2 should not be efficient as it leads to sterically hindered HH intermediate **14**, but polymerization may, in principle, be initiated by sterically less demanding initiator **9** or other initiators that have no alkyl substituents at the "*ortho*" position to Ni, e.g., Ph-Ni(L_2)-Br. These hypotheses will be verified in the present work.

2.2. KCTP of "Regular" Monomer 2. *In situ* ^{31}P NMR spectroscopy was used in this work to check the formation of intermediates shown in Scheme 1 and to compare the reactivity of monomers **1**−**4**. This method is a powerful tool for the investigation of the GRIM polymerization mechanism as demonstrated in recent papers of Lanni and McNeil which studied transformations of the mixture of isomeric monomers **1** and **2** in the presence of Ni(dppe)Cl_2[24a] and Ni(dppp)Cl_2.[24b] By conducting ^{31}P NMR experiments at lowered temperature, Lanni and McNeil[24a] were able to detect a catalyst-resting state **15** as well as a "living chain end" **16** (Scheme 1B). Intermediate **15** was the major compound at incomplete consumption of monomers showing that RE is the rate-limiting step here, whereas **16** became the predominant one at the end of polymerization when monomer **2** was already consumed.

We started our study with performing NMR experiments similar to those reported in ref 24 but using individual monomers **1** and **2** instead of their mixture, which were prepared from corresponding I/Br-precursors (Lanni and McNeil used 2,5-dibromo-3-hexylthiophene as the precursor). As the general polymerization behavior was already revealed in prior works, we were more interested to study early stages of KCTP. In addition to intermediates found previously,[24] product of the first transmetalation **5** (Scheme 1B) was also detected by *in situ* ^{31}P NMR at −20 °C (two doublets at 59.2 and 43.9 ppm, J = 39.7 Hz) when 1 equiv of **2** was added to dispersion of Ni(dppe)Cl_2 in THF-d_8 (Figure 1a). Furthermore, the symmetric intermediate **6** (51.4 ppm, singlet) was formed in smaller quantities by reaction of **5** with **2**.

To continuously monitor polymerization course, Ni(dppe)Cl_2 was mixed with 20 equiv of **2** at −20 °C, and a set of ^{31}P and ^{1}H spectra were recorded. At the beginning of the reaction (Figure 1b) Ni(dppe)Cl_2 was converted to initiator **6**

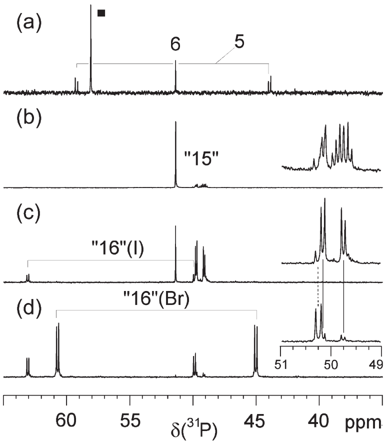


Figure 1. ^{31}P NMR spectra (THF-d_8, −20 °C) obtained (a) after addition of 1 equiv of **2** to dispersion of Ni(dppe)Cl_2 showing signals of Ni(dppe)Cl_2 (●) and the Th−Ni complexes **5** and **6** and (b−d) after addition of 20 equiv of **2** to dispersion of Ni(dppe)Cl_2 at different conversions of **2** showing signals of the "catalyst resting" "**15**" and of "living ends" "**16**".

but several signals in the 49−51 ppm region (AB spin systems caused by two nonequivalent but similar Th ligands) which are caused by "catalyst-resting" structure **15** having on one side short but different length oligothiophene chains which indicates the polymer growth. With the conversion increase and thus length of the P3HT chain, it is no more possible to distinguish different DP for this resting species, and accordingly only one AB spin system (49.8 and 49.2 ppm, J = 22.0 Hz) is observed (Figure 1c). It is noteworthy that for low-temperature polymerizations (e.g., −20 °C) complex **6** formed from Ni(dppe)Cl_2, and two monomer molecules were present in substantial quantities even at relatively high conversions of **2** (i.e., ∼50%), when a large amount of polymer was already formed. This is due to the slow initiation of the polymerization at low temperatures caused by the low solubility of Ni(dppe)Cl_2.[32] An accumulation of two doublets at 63.1 and 49.9 ppm (J = 33.6 ppm) which was not observed previously for polymerization of 2,5-dibromo-3-hexylthiophene-derived monomers[24] is also noteworthy. We ascribe these signals to $(Th)_n$-Ni(dppe)-I adducts formed by exchange of the Br atom of the "living" chain into I atom. The presence of I ions in the reaction mixture is due to a partial decomposition of *tert*Bu-I, which is a side product of the GRIM preparation of the monomer. As will be shown below, this halogen-exchange reaction is a fairly general process for Th-Ni(L_2)-X complexes, and stability of those complexes increases in the halogen range Cl < Br < I. Thus, one has to take into account this halogen-exchange process when interpreting ^{31}P spectra. The spectrum obtained at nearly complete monomer conversion (Figure 1d) is dominated by the signals of the "living" ends (Br- and I-form) (mainly $(Th)_n$-Ni(dppe)-Br; two doublets at 60.7 and 45.1 ppm, J = 35.5 Hz) and only small signals of "resting" polymer chains. This is in accordance with data of Lanni and McNeil, that **15** is the major intermediate in the middle and **16** is the major intermediate at the end of polymerization (for simplicity, only the shortest intermediates **15** and **16** are shown in Scheme S1, Supporting Information). Thus, it was possible to resolve initial Ni complexes **5** and **6** as well as other intermediates formed upon polymerization of "regular" monomer **2** (Scheme 1), and this information is helpful for investigation of reactivity of other monomers **1**, **3**, and **4**.

2.3. KCTP of "Disubstituted" Monomer 3. Attempts to involve monomer **3** (Scheme 2) into GRIM polymerization were undertaken earlier. In particular, Frechet et al. aimed at the preparation of P3HT with reduced regioregularity and tried to copolymerize **2** and **3** at a low content of **3**.[33] A small fraction of **3** (∼2%) was detected in the resulting copolymer; however, it was not clear whether the content of **3** in the copolymer can be substantially increased and whether homopolymerization of **3** under GRIM conditions is possible. In the present work, **3** was prepared from 2-bromo-3,4-hexyl-5-iodothiophene and *tert*-butylmagnesium chloride (*tert*-Bu-MgCl), and afterward KCTP was attempted at room temperature using Ni(dppp)Cl_2. We found that monomer **3** is essentially inert even at prolonged (24 h) stirring, and the respective protonated product was recovered after hydrolysis (Table 1, entry 14). It was previously reported that transmetalation is the rate-limiting step if Ni(dppp)Cl_2 is used for the synthesis of P3HT,[2b] and the reductive elimination is the rate-limiting step when Ni(dppe)Cl_2 is used; yet, the polymerization proceeds much faster with dppe.[24] This suggests that dppe-ligated Ni complexes are more active at the transmetalation step, and thus, they should be more efficient in polymerizations of monomers with more sterically hindered magnesium ends. With this in mind, we further attempted polymerization of **3** using Ni(dppe)Cl_2 or Ph-Ni(dppe)-Br but found that no polymerization at room temperature occurred in these cases as well.

To reveal the "bottleneck" problem of the polymerization of **3**, *in situ* ^{31}P NMR measurements were performed. The product of the first transmetalation **23-Cl** was observed when Ni(dppe)Cl_2 was mixed with 20 equiv of **3** but also the signals of **23-I** (Figure 2a). To prove the structure of the formed complexes, **23-Cl**, **23-Br**, and **23-I** were independently synthesized from the corresponding Ni(dppe)X_2 salts and an equimolar amount of **3** (Figure 2b−d). It was also found that **23-Cl** easily exchanges Cl atom with Br or I forming **23-Br** or **23-I**, if the corresponding salts are present in reaction mixture. Some amounts of iodine salts are present due to partial decomposition of *tert*Bu-I, which is a byproduct of GRIM procedure. If a large excess of **3** is added to Ni(dppe)Cl_2, the quantity of iodine salts accumulated is sufficient to convert a substantial fraction of **23-Cl** into **23-I.** However, **23-Cl** was the only product when Ni(dppe)Cl_2 was mixed with 2 equiv of **3**. It is noteworthy that in the case of regular monomer **2** the product of the first transmetalation was possible to detect only when Ni(dppe)Cl_2 was used in excess, since the second transmetalation was very quick.

These results clearly demonstrate that the presence of the alkyl substituent at the magnesium end prohibits transmetalation if a second alkyl substituent is also present at the "*ortho*" position to the Ni center so that the intermediate **24** cannot be formed.[34] It is also noteworthy that the alkyl substituent is also present at the bromine end of **3**; however, this "*ortho*" substituent, obviously, does not promote the next RE and OA steps and the polymerization in general, as previously proposed.[30]

2.4. KCTP of "Reverse" Monomer 1. It should be noted that polymerizations of monomer **1** initiated by Ni(dppp)Cl_2 and Ph-Ni(dppp)-Cl were earlier attempted by Luscombe et al.,[30] and no corresponding polymers were obtained in both cases. The results obtained with Ni(dppp)Cl_2 were in accordance with our expectations; however, unreactivity of **1** in the presence Ph-Ni(dppp)-Cl was surprising for us.[31] As discussed in section 2.1, Scheme 2. **Disubstituted Monomer, 2-Bromo-5-chloromagnesio-3,4-dihexylthiophene (3, R = Hex), Is Not Reactive under Kumada Catalyst-Transfer Polycondensation Conditions Whereas Unsubstituted Monomer, 2-Bromo-5-chloromagnesiothiophene (4), Polymerizes Smoothly under the Same Conditions**

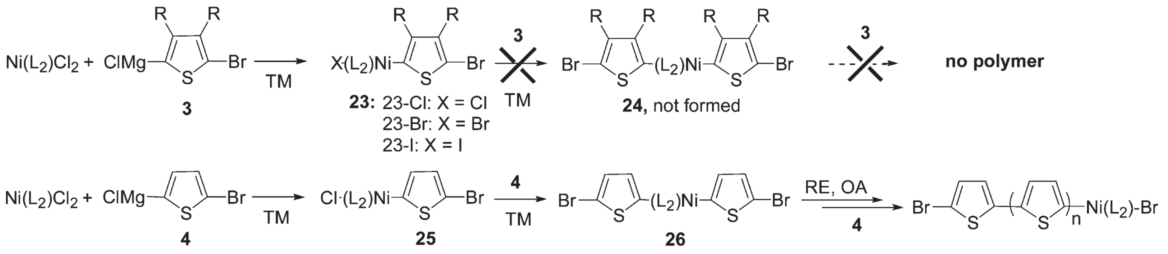


Table 1. **Polymerization Results**

entry	monomer	initiator	monomer/init	conversion, %/time	M_n (GPC)	PDI
1	**1**	Ni(dppe)Cl_2	40	no polymerization/24 h		
2	**1** (97%) + **2** (3%)	Ni(dppe)Cl_2	40	50%/1.5 h	<30000	2.3
3	**1**	Ph-Ni(dppe)-Br	40	60%/5 min		
4	**1**	Ph-Ni(dppe)-Br	40	95%/15 min	6700	1.29
5	**1**	Ni(dppp)Cl_2	30	no polymerization/24 h		
6	**1** (97%) + **2** (3%)	Ni(dppp)Cl_2	30	18%/1 h		
7	**1** (97%) + **2** (3%)	Ni(dppp)Cl_2	30	27%/5 h		
8	**1** (97%) + **2** (3%)	Ni(dppp)Cl_2	30	38%/24 h	19000	2.1
9	**1**	Ph-Ni(dppp)-Br	30	30%/2 h		
10	**1**	Ph-Ni(dppp)-Br	30	70%/5 h	3900	1.22
11	**1** (97%) + **2** (3%)	Ph-Ni(dppp)-Br	30	<10%/24 h		
12	**2**	Ph-Ni(dppe)-Br	40	95%/5 min	7100	1.15
13	**2**	Ph-Ni(dppp)-Br	30	95%/10 min	7300	1.09
14	**3**	all types		no polymerization/>24 h		
15	**2a** (60%)+**4** (3%)	Ph-Ni(dppe)-Br	50	80%/30 min	9100	1.27

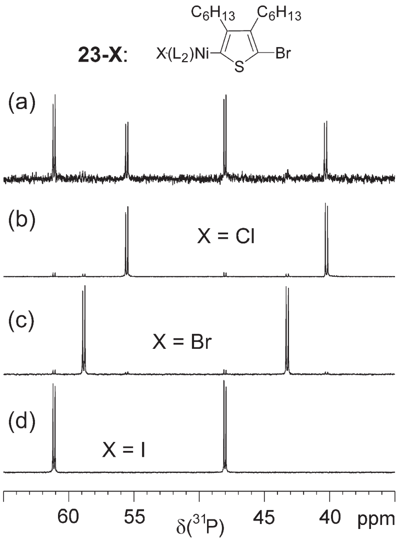


Figure 2. ${}^{31}P$ NMR spectra of (a) the reaction mixture of Ni(dppe)Cl_2 and 20 equiv of **3**, (b) **23-Cl** (55.6 and 40.2 ppm, $J = 36.0$ Hz), (c) **23-Br** (58.9 and 43.3 ppm, $J = 34.6$ ppm), and (d) **23-I** (61.1 and 48.0 ppm, $J = 31.9$ Hz) in THF-d_8 at 30 °C.

initiation of the polymerization of pure **1** should be problematic with Ni(dppp)Cl_2 or Ni(dppe)Cl_2 catalysts because the second TM step leads to the sterically hindered HH-intermediate **13**. However, the chain propagation itself is not necessarily impossible since polymerization of **1** proceeds via sterically "allowed" TH-intermediate **19**. Thus, one can expect that **1** may be polymerized by sterically not demanding Ph-Ni(dppe)-Br or Ph-Ni(dppp)-Br initiators.

It is noteworthy that the preparation of **1** with high purity was problematic in our hands. First, we attempted the previously reported procedure to synthesize 5-bromo-3-hexyl-2-iodothiophene (**27**) (the key intermediate toward **1**) via selective lithiation of 3-hexylthiophene (**28**) at the 5-position of the thiophene ring using sterically hindered superbases. However, we failed to selectively carry out this reaction, even after some optimization of reaction conditions, such as temperature and choice of bases. The separation of isomeric 5-bromo-3-hexylthiophene (**29**) from 2-bromo-3-hexylthiophene (**30**), which always formed in the reaction was also problematic in our hands. Alternatively, **27** was prepared by a standard two-step halogenation of **27**. The first halogenation of **28** with iodosuccinimide was selective and led to desired 3-hexyl-2-iodothiophene (**31**) with almost 100% purity. However, the next bromination of **31** using bromosuccinimide was accompanied by partial I to Br substitution, so that the resulting product **27** was contaminated with about 5% of 2,5-dibromo-3-hexylthiophene (**32**) (Figure S1, Supporting Information). If an equimolar amount of *tert*-BuMgCl was subjected to GRIM with this impure **27**, then the reversed monomer **1** was contaminated by the regular monomer **2** (Figure S2). Fortunately, it was possible to prepare pure **1** at

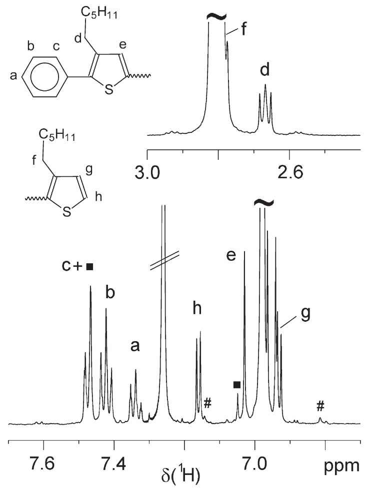


Figure 3. ^{1}H NMR spectrum of Ph-poly**1**. Signals marked with ■ and # are ^{13}C satellites of residual $CHCl_3$ in the solvent $CDCl_3$ and of the aromatic P3HT backbone signal, respectively.

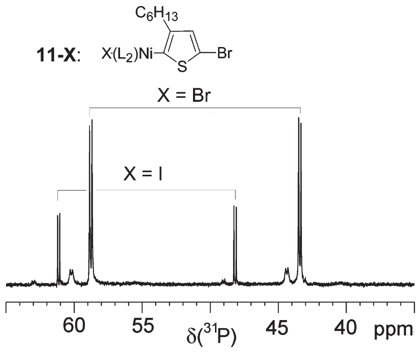


Figure 4. ^{31}P NMR spectrum of the reaction mixture of Ni(dppe)Cl_2 and 10 equiv of **1** in THF-d_8 at 30 °C showing signals of monotransmetalation products **11-Br** (58.8 and 43.4 ppm, J = 35.7 Hz) and **11-I** (61.1 and 48.2 ppm, J = 33.6 Hz) and of propagating chain ends.

low temperature using less than 1 equiv of *tert*-Bu-MgCl (~0.94 equiv) relative to the monomers since iodine is more reactive than bromine (Figure S3). In the experiments described below, both **1** contaminated by **2** (<4%) and **1** not contaminated by **2** were used.

Addition of Ph-Ni(dppe)-Br to either pure **1** or **1** containing 2—4% of **2** led to a rapid polymerization of **1**. As a typical example, Figure 3 shows a ^{1}H NMR spectrum of Ph-P3HT obtained from **1** containing ~3% of **2** at 40/1 monomer/initiator ratio. Although no detailed kinetic studies were performed, preliminary results show that polymerization of monomers **1** and **2** proceeds with approximately the same rate (thus, 60% of **1** is consumed within 5 min (giving P3HT with DP ~ 40), and conversion of **1** was almost complete in 15 min; Table 1, entry 4). Almost complete incorporation of the Ph group was found by the integration of the end and starting groups, and a narrowly distributed polymer was obtained (GPC data: PDI = 1.29, M_n = 6700 g/mol). In full agreement with the polymerization mechanism, the starting Ph group in the resulting polymer was connected to the head-oriented 3-hexylthiophene unit (Figure 3) which is the reversed connection compared to the starting group structure in Ph-P3HT prepared earlier from **2**.[3,14,16] It is noteworthy that Ph-Ni(dppe)-Br-initiated polymerizations proceeded smoothly not only with the pure monomer **1** but also with the monomer containing ~3% of **2**.

Pure monomer **1** did not polymerize in the presence of Ni(dppe)Cl_2. When Ni(dppe)Cl_2 was used to polymerize monomer **1** containing ~3% of **2**, low conversion of **1** was achieved even after prolonged stirring (~50% for 90 min, Table 1, entry 2). A polymeric product formed was poorly soluble even in boiling chloroform, which is characteristic for P3HTs with MWs well above 30 000 g/mol (GPC measurements failed to give reliable MW for these high MW polymers). Such results are consistent with a slow initiation/fast propagation scenario suggestive, in turn, that the polymerization was not initiated by all Ni(dppe)Cl_2 added to the reaction mixture, but rather by a small part of it. This is in accordance with the initiation mechanism discussed in section 2.1 (Scheme 1B). In particular, we suppose that the major part of Ni(dppe)Cl_2 underwent the first TM with **1**, as it is the major Grignard compound present in the reaction mixture. The resulting intermediate **11** should be inactive in the second TM step with the second equivalent of **1** since this leads to the sterically unfavored HH-coupling product **12**. This is confirmed by *in situ* ^{31}P NMR measurements (Figure 4). Although a large excess of **1** (10 equiv) relative to Ni(dppe)Cl_2 was added in this NMR experiment, **11** was the predominant product here (as it was for the monomer **3**, Cl atom in **11-Cl** underwent fast exchange with bromine and iodine salts to give **11-Br** and **11-I**), and no singlet indicating the formation of **12** could be proved. Two pairs of broadened doublets at 60.2 and 44.4 ppm (J = 34.5 Hz) and 49.0 and 63.0 (J ~ 33 Hz) that could be assigned to the propagating chain end (such as **21** with X = Br and I, respectively) were observed only in trace amounts. These "trace" signals correspond to a side-polymerization process leading to insoluble, high-MW P3HT as follows. Although the intermediate **11** is not reactive toward **1**, it can react with **2** if such monomer is present in the reaction mixture. Thus, if "impure" monomer **1** is subjected to polymerization, intermediate **11** accumulated in the first step should reacts with the monomer **2** giving **7** and, after RE/OA steps, the initiators **10** and **9** as shown in Scheme 1B. We therefore believe that the sterically nonhindered initiator **9** initiates polymerization of **1**. According to this mechanism, the formation of the initiators **9** and **10** is a very slow process, since it is controlled by the concentration of **2**, which is about 2 orders of magnitude lower than concentrations of monomers usually used for conventional GRIM polymerizations. The influence of the slow initiation process on the MW and MW distribution is especially critical in polymerizations catalyzed by dppe-ligated complexes as the chain propagation proceeds much faster here compared to dppp-ligated catalysts. Thus, in the above-considered polymerization of the "impure" **1** in the presence of Ni(dppe)Cl_2 there is a typical situation of the slow initiation/fast propagation resulting into high-MW polymers, with the MW being controlled by the polymer solubility limit rather than by the monomer/initiator ratio.

In the next step, polymerization of the monomer **1** was investigated in the presence of dppp-ligated initiators. We found that the pure monomer **1** does not polymerize in the presence of Ni(dppp)Cl_2 even at prolonged (during 24 h) stirring at room temperature, in accordance with the previously published report.[30] However, the "impure" monomer **1** containing 3% of **2** polymerized slow at RT when mixed with Ni(dppp)Cl_2 in a 30/1 ratio. Thus, conversion of the monomer **1** of about 18, 27, and 38% was observed for polymerizations conducted for 1, 5, and 24 h, respectively (Table 1, entries 6—8). As should be expected for the polymerization of the reversed monomer **1**, the ^{1}H NMR spectrum of the resulting P3HT contains the characteristic doublet at 7.15 ppm of the terminal hydrogen atom,[34] which is not observed in the spectra of P3HT formed upon polymerization of the regular monomer **2**. The resulting polymer possessed a very high MW of $M_n \sim 19000$ g/mol (considering the initial 30/1 monomer-to-catalyst ratio), which is the sign of a slow initiation. This is consistent with the assumption that the polymerization was initiated by the asymmetric initiators **9** and **10** (Scheme 1) formed from **1**, **2**, and Ni(dppp)Cl_2.

The pure monomer **1** polymerized much more efficiently with Ph-Ni(dppp)-Br than with Ni(dppp)Cl_2; however, this polymerization was ~50 times slower than the polymerization of **2** under otherwise identical conditions (Table 1, entries 9 and 10). In particular, in the polymerization conducted at 30/1 monomer/initiator ratio, ~30% of the monomer was converted within 2 h; the highest monomer conversion of ~70% was achieved at a prolonged stirring (5 h) leading to phenyl-terminated P3HT with DP ~ 20 (NMR data), M_n = 3900 g/mol, and PDI = 1.22 (GPC data). Furthermore, a high sensitivity of polymerization results on the purity of **1** was observed for the Ph-Ni(dppp)-Br-initiated polymerization, but not for the Ph-Ni(dppe)-Br-initiated one discussed above. In particular, Ph-Ni(dppp)-Br-initiated polymerization of **1** was almost fully suppressed in the presence of 3% of **2** (polymerization conducted for 24 h resulted into Ph-P3HT with a yield <10%; Table 1, entry 11). We explain this by a very low reactivity of **1** toward Ph-Ni(dppp)-Br so that Ph-Ni(dppp)-Br undergoes selective TM with **2** present in the mixture as the impurity, giving sterically hindered Ni species which are unable to initiate polymerization of **1** (Scheme S4). This assumption was confirmed by ^{1}H NMR analysis of the reaction mixture, which reveals that the coupling of Ph-Ni(dppp)-Br with **2** into **34** was indeed the major reaction pathway in this case and compound **33** was not formed among the reaction products (Supporting Information, Scheme S2 and Figure S4).

As can be seen from these results, the reactivity of the reversed monomer **1** differs significantly in polymerizations initiated by dppp- and dppe-ligated catalysts. Thus, the reversed monomer **1** and the regular monomer **2** polymerize with approximately the same rates in KCTP catalyzed by the dppe-ligated catalyst. On the other hand, **1** polymerizes ~50 times slower than **2** in the polymerization catalyzed by the dppp-ligated catalyst (Table 1, entries 10 vs 13). Although polymerizations of both monomers formally proceed via the same (or similar) *intermediate* 7 having either a TH or HT structure (Scheme 1B), steric hindrances occurring in the *transition states* preceding those intermediates are obviously different in polymerizations of **1** and **2** catalyzed by dppp-ligated complexes. It is obvious that the HT coupling occurs faster for monomers which approach to sterically hindered Ni centers by their sterically nonhindered magnesium ends (e.g., as in **11** + **2**, Scheme 1) than the opposite coupling mode when monomers having sterically hindered magnesium ends attack sterically nonhindered Ni centers (e.g., as in **5** + **1**, Scheme 1). We propose that the alkyl substituents *ortho* to the magnesium center impede the TM stronger than the substituents *ortho* to the Ni center, since Grignard reagents are more prone to aggregation which further increases steric hindrances. Naturally, these steric hindrances occurring at the TM step have influence on polymerization rates (of **1** vs **2**) only in the case of dppp-ligated KCTP for which the TM step is the rate-determining step.

The observed influence of alkyl substitution pattern on reactivity of thiophene-based monomers in KCTP is qualitatively similar to a trend observed in Kumada cross-coupling of small-molecule aryl halides and aryl Grignard reagents. It was documented by Kumada et al. that sterically hindered *ortho*-substituted aryl halides couple smoothly with aryl Grignard reagents, suggesting that *ortho* substituents in aryl halides hamper the coupling to much lesser extend than *ortho* substituents in aryl Grignard reagents.[35] For instance, Ni-catalyzed Kumada coupling of aryl halides with sterically hindered aryl Grignard reagents proceeds much slower and with lower yields than with sterically not hindered counterparts, especially for couplings with catalysts ligated with bidentate phosphorus ligands. Thus, no coupling was observed between Mes-MgCl (Mes = mesityl) and PhBr using dppe-ligated catalyst, and the coupling proceeded with moderate yields (78%) upon prolonged reflux (20 h) in THF with dppp-ligated catalyst. At the same time, the coupling between sterically not hindered aryl Grignard reagents and PhBr proceeds within minutes at room temperature. A similar trend was found by McCullough et al. for the coupling of model alkyl-substituted thiophene bromides and alkyl-substituted thiophenic Grignard componds. Thus, coupling of sterically hindered Grignard reagent with sterically hindered 2-bromo-3-thiophene proceeded very slow even at reflux in THF and resulted in a corresponding HH-coupled adduct with about 10% yield.[29] It is, however, noteworthy that the coupling of 2-bromo-3-thiophene and sterically not hindered Grignard was also slow and inefficient, suggesting that *inter*molecular OA of Ni(0) thienyl halides is sensitive to steric hindrances at the C—Br bond (this is obviously not valid for phenyl halides investigated by Kumada et al.[35]).

KCTP of "Unsubstituted" Monomer 4. We further studied the polymerization of the unsubstituted monomer **4** obtained via GRIM from 2,5-dibromothiophene and *tert*-Bu-MgCl. Unsubstituted monomer **4**, like reactive monomer **2**, has no substituent at the magnesium end and hence should be reactive at the TM step. However, like **1**, it does not have any substituent at the bromine end, and the propagating Ni complex is not stabilized here by the "*ortho*" substituent; thus, the role of this factor on the performance of the polymerization could be further elucidated. Monomer **4** was previously used by McCullough et al. for the preparation of poly(3-dodecylthiophene)-*b*-polythiophene-*b*-poly(3-dodecylthiophene) triblock copolymers,[2b] so its general reactivity under GRIM conditions has already been shown. It was further reported that a low-MW tailing was observed in the GPC traces of the resulting triblock copolymer, indicating the presence of some dead or inactive chains during the chain extension process. It was however unclear whether the decreased polymerization performance is related only to the low solubility of the poly(3-dodecylthiophene)-*b*-polythiophene, causing the precipitation of the nickel-terminated polymer, or whether this is due to the absence of the "*ortho*" stabilization in the propagating Ni complex.[30]

Polymerizations of **4** initiated by Ni(dppe)Cl_2 at two different initiator-to-monomer ratios of 50/1 and 10/1 were performed which led to fast (<10 min) and a near complete consumption of **4** in both cases. A purple product obtained at 50/1 feed ratio was neither soluble nor dispersible in common organic solvents, suggesting that the product is unsubstituted polythiophene (PT) with MW higher than the solubility limit. In contrast, a red product was formed at 10/1 feed ratio. Although also insoluble, it formed a stable dispersion in chloroform that allowed recording of its UV—vis and emission spectra (Figure S8). Absorption spectrum (λ_{max} = 415 nm, shoulders: 510 and 600 nm) and emission spectrum (λ_{max} = 485 and 514 at 415 nm excitation wavelength; λ_{max} = 615 nm, shoulder: 663 at 518 nm excitation wavelength) are characteristic for PT oligomers. The observed trend, namely that the lower MW product was obtained at the lower initiator/monomer ratio, is consistent with the assumption that polymerization of **4** proceeds via the chain-growth catalyst-transfer mechanism, similarly to polymerization of **2**.

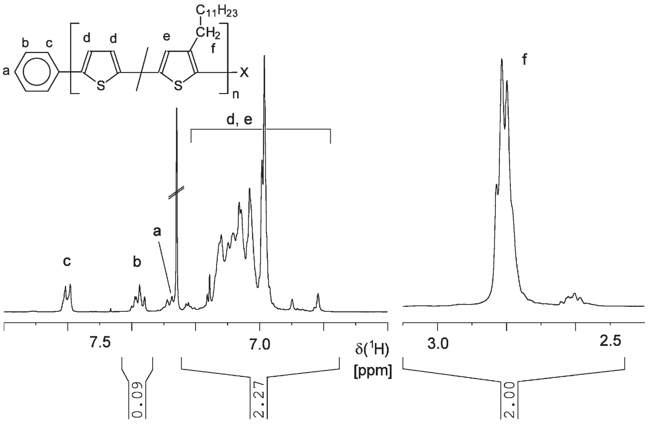


Figure 5. ^{1}H NMR spectrum (region) of poly(thiophene-*co*-3-dodecylthiophene), P(3DT-*co*-T), in $CDCl_3$ (61 mol % DT, 39 mol % T; n ∼ 36; X = H and Br).

To circumvent solubility problems, **4** was copolymerized with 2-bromo-5-chloromagnesio-3-dodecylthiophene, **2a**, having a relatively large dodecyl substituent. Copolymerization of **4** and **2a** was performed using externally added Ph-Ni(dppe)-Br initiator. The initiator was added to the polymerization mixture in solution to ensure a simultaneous initiation of all Ph-Ni(dppe)-Br species. The copolymerization of **2a**/**4** mixture led to Ph-terminated poly(3-dodecylthiophene-*co*-thiophene), Ph-P(3DT-*co*-T), with the ratio between 3DT and T units in the copolymer roughly corresponding to the [**2a**]/[**4**] feed ratio. No depletion of one of the monomers in the mixture during polymerization was found, suggestive similar polymerization rates of **2a** and **4**. As a typical example, we consider a polymerization performed at [**2a**]/[**4**] = 3/2, [**2a**] + [**4**]/[Ph-Ni(dppe)-Br] ratio of 50/1 and ∼80% conversion of monomers (Table 1, entry 15). The obtained Ph-P(3DT-*co*-T) had a monomodal GPC trace with M_n = 9100 g/mol and PDI = 1.27. Assuming that all chains were initiated by Ph-starting groups, the evaluation of the ^{1}H NMR signal integrals gave a degree of polymerization (DP) of 36 (Figure 5).

To get a deeper insight into the polymerization mechanism, surface-initiated Kumada catalyst-transfer polycondensation (SI-KCTP) of **4**, **2a**, and their mixtures was performed from organosilica microparticles. It was previously demonstrated that SI-KCTP is a useful tool to study the chain-growth performance.[16,17] In particular, this method allows an easy separation of surface-grafted and freely dissolved polymers and thus quantitatively compares the amount of the polymer that was obtained via the perfect chain-growth process (corresponding to surface-grafted polymer) from reinitiated polymerization products. To this end, monodisperse (∼880 nm in diameter) silica particles having an approximately ∼10 nm thick organosilica shell were prepared via sequential sol−gel hydrolysis of tetramethyl orthosilicates (TMOS) and [2-(4-bromophenyl)-ethyl]triethoxysilane, as described previously.[16,17] The latter silane provides a useful functionality on the surface of the particles, which is required for catalyst immobilization. Initiating sites were developed by treating of the particles consecutively with $Et_2Ni(bipy)$ and dppe (Scheme S3). Prior to SI-KCTP, the particles were carefully purified from physisorbed Ni compounds by several centrifugation/redispersion cycles using anhydrous and degassed THF in an argon atmosphere. To perform SI-KCTP, monomers **4**, **2a**, or their mixtures were added to the dispersion of the activated particles, and the polymerizations were performed at room temperature (RT) for 20 min. Afterward, the resulting composite particles were carefully separated by repeated redispersion/centrifugation cycles from any ungrafted polymers, catalyst, and byproducts. Although homopolymerization of **4** initiated by $Ni(dppe)Cl_2$ results in neither soluble nor dispersible materials, the grafting from microparticles leads to composite particles (further designated as μ-PT particles) that are easily dispersible in chloroform or THF. These burgundy-red dispersions are stable at concentrations up to 5 mg/mL for several months. The diameter of the particles, as determined by SEM, increased upon grafting of PT from 880 nm for starting unmodified particles up to 920 nm for μ-PT particles (Figure S6). Although the surface roughness increased after the grafting, it remained quite uniform, highlighting the advantages of this grafting method in comparison with other methods.[18]

Grafting experiments were also performed for mixtures of **4** and **2a** in different ratios, including the mixtures polymerization of which in bulk solution results into soluble copolymers, conditions already used in bulk polymerizations. In all cases, the grafting processes were successful, and only minor amounts of ungrafted copolymers were recovered in the experiments emphasizing a good chain-growth performance at any **4**/**2a** ratio used. It is also important to emphasize that in some grafting experiments we used a large excess of the monomer **4** respective to the amount of the Ni-initiator immobilized on the surface of the organosilica particles. A large quantity of (protonated) monomer was recovered from these experiments besides the hairy particles, and virtually no ungrafted PT was formed. The fact that not the whole quantity of the monomer was consumed further suggests that virtually no reinitiation reactions took place under these conditions. This is in contrast with SI-KCTP of polyfluorenes where distinct termination and reinitiation reactions were previously observed.[17] Thus, we can tentatively propose that the relatively poor performance of the chain-growth polymerization of the fluorene-based monomer[17] does not arise from the absence of alkyl substituent at the bromine end but is due to other factors, e.g., the lack of heteroatoms stabilizing intermediate Ni(0) complexes, or larger molecular length, or lesser purity of the monomer.

According to thermal gravimetric analysis (TGA), the resulting μ-PT particles and the particles with grafted P(3DT-*co*-T) copolymer shells loose 10−12% of their weight in the temperature interval from 450 to 600 °C in an oxygen atmosphere (that is a typical decomposition behavior of PT). For the given particle size and densities of the components, the PT (or poly(3DT-*co*-T)) content in the particles corresponds to the thickness of polymer shells, h, from 25 to 30 nm (Figure S9). This is a typical shell thickness for other polythiophene hairy particles, e.g., for P3HT hairy particles studied in our lab previously.[16] Thus, we did not find any substantial difference in the grafting behavior of alkyl-substituted and unsubstituted thiophene-based monomers, suggesting that stabilization of the propagating Ni complexes by "*ortho*" substituents is not strictly necessary for achieving a clean chain-growth Kumada polycondensation. It was previously found that the absence of alkyl substituents in the position adjacent to the C−Br end group promotes chain-termination processes during KCTP initiated by Ni initiators ligated by *monodentate* phosphine ligands.[3] Ni complexes with monodentate phosphine ligands generally exhibit a much worse polymerization performance than Ni catalysts ligated by *bidentate* phosphine ligands. Thus, we can tentatively conclude that the *ortho* stabilization is more important for poorly performing Ni complexes ligated by *monodentate* ligands.

It is noteworthy that the absorption spectrum of the dispersion of the μ-PT particles in chloroform (λ_{max} = 554 and 600 nm, shoulder: 515 nm, Figure 6a) resembles the spectrum of regioregular HT P3HT in the solid state and is only slightly blue-shifted.

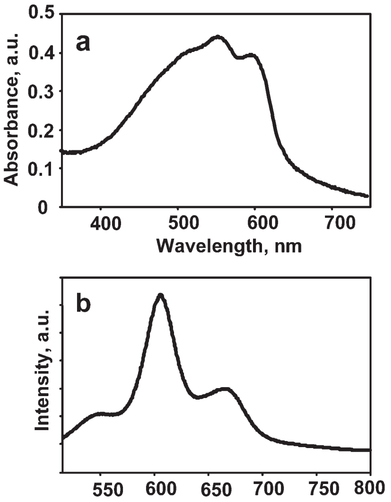


Figure 6. (a) UV−vis and fluorescence (b) spectra of the dispersion of the μ-PT particles in chloroform.

Emission spectrum of the μ-PT particles is also well-structured (λ_{max} = 550, 619, and 678 nm, Figure 6b). The appearance of structured spectral features reflects an important planarization of the polymer chains and the formation of ordered phases similar to those observed in HT P3HT films.[36] This result can be attributed to the fact that the polymer chains are relatively stretched and approach closely to each other within the densely grafted brush layers that facilitates planarization and aggregation of polymer chains within the brush.

3. CONCLUSION

The reactivity of differently substituted alkylthiophenic monomers ClMg-Th(R)-Br under Ni-catalyzed Grignard metathesis (GRIM)/Kumada catalyst transfer polycondensation (KCTP) conditions was investigated. Transmetalation (TM) was found to be a key step defining the ability of alkyl-substituted thiophene-based ClMg-Th(R)-Br monomers to be polymerized under Ni-catalyzed GRIM/KCTP conditions. A chain propagation is prohibited if TM step leads to sterically hindered head-to-head (HH) Th(R)-Ni-(R)Th intermediates in which alkyl substituents in both thienyl rings are in the "*ortho*" position relative to the Ni center. However, polymerization proceeds smoothly if no alkyl substituents are present in at least one "*ortho*" position relative to the Ni center, such as in head-to-tail (HT) Th(R)-Ni-Th(R), tail-to-head (TH) (R)Th-Ni-(R)Th, tail-to-tail (TT) (R)Th-Ni-Th(R), or unsubstituted Th-Ni-Th intermediates. This rule is always fulfilled for the "regular" monomer 2-bromo-5-chloromagnesio-3-hexylthiophene (**2**) and the "unsubstituted" monomer 2-bromo-5-chloromagnesio-thiophene (**4**) since they have no alkyl substituents "*ortho*" to the magnesium end and thus easily polymerize in the presence of various Ni initiators. However, the "reversed" monomer 5-bromo-2-chloromagnesio-3-hexylthiophene (**1**) has a sterically hindered magnesium end, and therefore the initiation step is hampered with Ni(dppe)Cl_2 or Ni(dppp)Cl_2 initiator precursors but proceeds with sterically nonhindered Ph-Ni(dppe)-Br and Ph-Ni(dppp)-Br initiators or with initiators formed from Ni(dppe)Cl_2, 1 equiv of **1**, and 1 equiv of **2**. The chain propagation is also labored in the polymerization of the monomer **1** which has the alkyl substituent "*ortho*" to the magnesium end. This reactivity feature is more obvious with dppp-ligated catalysts as these are less active at the TM step. Thus, the polymerization of **1** with Ph-Ni(dppp)-Br initiator proceeds about 50 times slower than polymerization of **2** with the same initiator, whereas the dppe-ligated catalyst polymerizes **1** and **2** with approximately the same rate as it is more reactive (less selective). In accordance with the formulated rule, "disubstituted" 2-bromo-5-chloromagnesio-3,4-dihexylthiophene (**3**) does not polymerize by any initiators, but it undergoes monotransmetalation with Ni(dppe)Cl_2 as confirmed by *in situ* ^{31}P NMR measurements. "Unsubstituted" monomer **4** smoothly homopolymerizes and copolymerizes with 2-bromo-5-chloromagnesio-3-dodecylthiophene (**2a**) by various unsupported and surface-immobilized initiators via a perfect chain-growth mechanism, reflecting the unimportance of the "*ortho*" stabilization of the chain-propagating Ni species for achieving a good polymerization control, if Ni catalysts are ligated by bidentante dppp and dppe ligands. The obtained results demonstrate that unsubstituted thiophene is a suitable building block for designing of new conjugated polymers via chain-growth Kumada catalyst-transfer polycondensation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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