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Toward Perfect Control of End Groups and Polydispersity in Poly-(3-hexylthiophene) via Catalyst Transfer Polymerization

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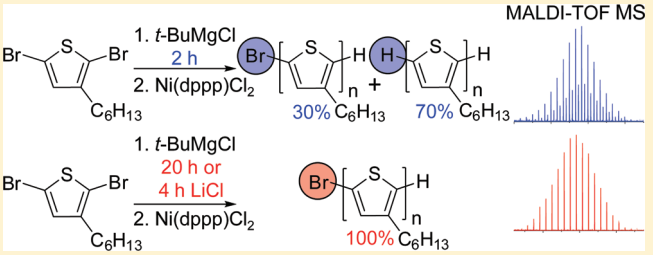
Supporting Information

ABSTRACT: We report the influence of the active Grignard monomer formation on the end groups and polydispersity of poly(3-hexylthiophene) (P3HT) for the catalyst transfer polymerization. The rate of the active Grignard monomer formation of 2,5-dibromo-3-hexylthiophene using *t*-BuMgCl was studied using ^{1}H NMR. Only in the absence of unreacted/excess *t*-BuMgCl, polymers with 100% H/Br end groups were formed. If the active Grignard monomer formation was incomplete and thus unreacted *t*-BuMgCl remained, the end groups depended on the polymerization time; the ratio of H/Br to H/H end groups decreased with increasing time. LiCl was shown to accelerate the active Grignard monomer formation but negatively affects the regioregularity to a small extent. It also increases the molecular weight of P3HT when used in combination with Ni(dppp)Cl_2 as a catalyst. Further, MeOH as a quenching reagent was identified to cause chain−chain coupling and hence an increase in the polydispersity. Thus, important parameters influencing the kinetics of the catalyst transfer polymerization were studied, and a series of P3HTs with 100% H/Br end groups and low polydispersities were synthesized by an optimized procedure. These findings are very relevant for extending this polymerization method to new monomers and for the realization of well-defined block copolymers.



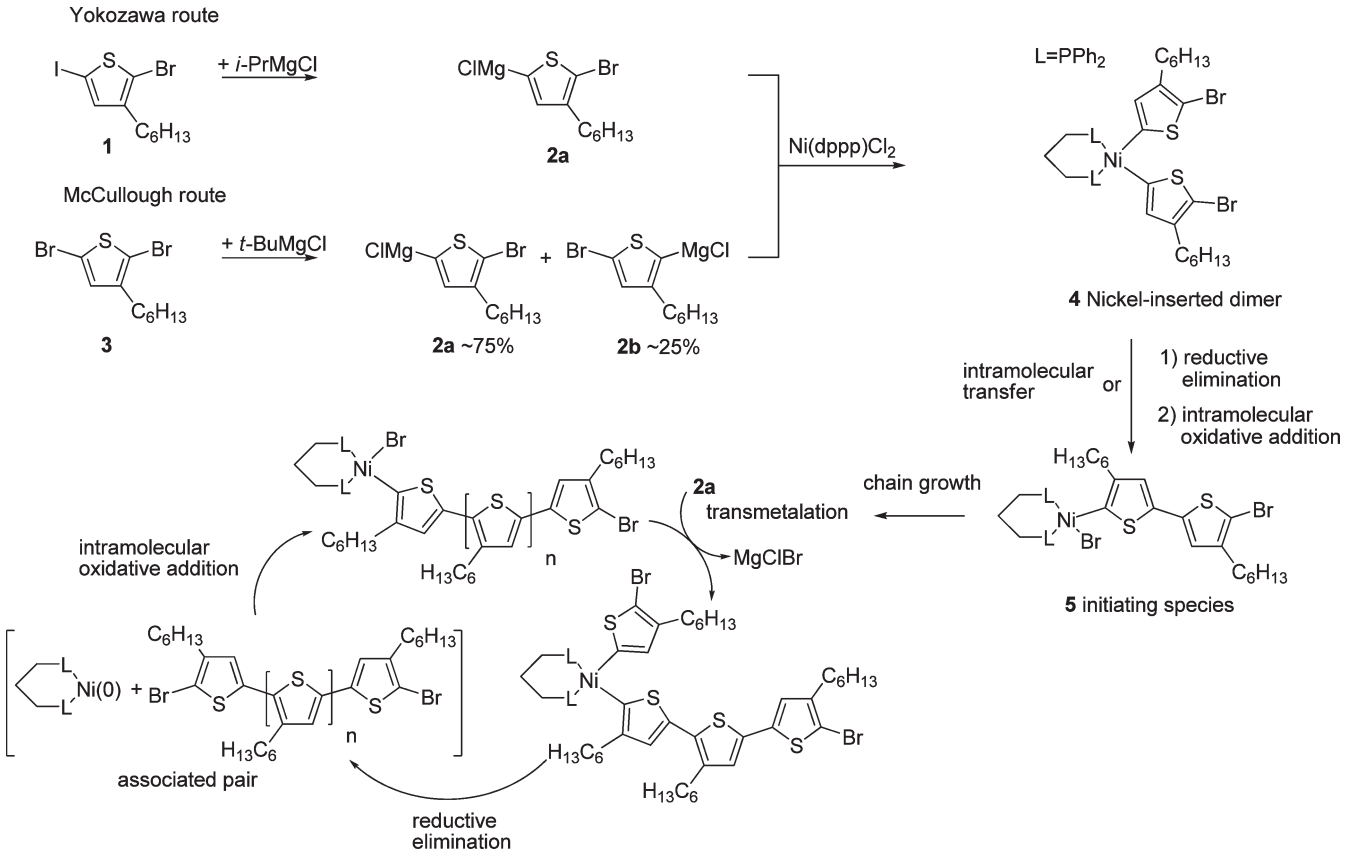
INTRODUCTION

Organic semiconductors and especially conjugated polymers are a prominent class of materials finding application in organic field effect transistors (OFETs)[1] or organic photovoltaics.[2] Poly(3-hexylthiophene) (P3HT) is one of the most common and prototype conjugated polymers used as a hole conductor in these devices. Its development, starting from unsubstituted insoluble poly(thiophenes) to irregular alkyl substitution to regioregular P3HT, reached a new level of control of polymerization with the discovery of a chain growth mechanism by Yokozawa and McCullough.[3−7] This allows for the synthesis of P3HTs with low polydispersities (PDIs) and adjustable molecular weights. The polymerization is called Grignard metathesis polymerization or catalyst transfer polycondensation/polymerization; the former name describes the formation of the monomer via metathesis reaction and the latter one the decisive step for the chain growth mechanism, namely the intramolecular transfer of the catalyst. In general, good control of well-defined end groups and molecular weights as well as low polydispersities is necessary to analyze the effect of molecular weight on the charge carrier mobility, to obtain block copolymers, or to tune the performance of such materials in organic solar cells.[8−13] Recently, this method of polymerization was extended to obtain a few other polymers such as poly(2,5-dihexyloxybenzene),[14] poly(alkylfluorene),[15,16] poly(*N*-dodecylpyrrole),[16] poly(*N*-octyl-2-carbazole),[16] and poly(2,3-dihexylthieno[3,4-*b*]pyrazine).[17] Also nonconjugated polymers like poly(bithienylmethylenes)[18] or oligomers[19] were successfully polymerized. Additionally, new approaches allowed for surface initiated polymerization and the synthesis of brushes.[20,21]

In all cases, the polymerization proceeds via the active Grignard monomer formed from its dihalide. Therefore, the conditions of active monomer formation and its polymerization decide the final polymer structure, molecular weight, and PDI. Thus, detailed understanding of kinetics is necessary to extend this valuable method toward relevant new monomers. A lot of factors have been identified which influence the structure and PDI of the polymers or the success of the chain growth polymerization: for example, the additives,[14,16,22] the position of the substituent on the aromatic core,[23] the metal,[24] and the ligand of the catalyst used.[22,24−27] To establish a universal chain growth polymerization for conjugated polymers, it is essential to identify all parameters that affect the kinetics and nature of the resulting polymers. Thus, the following relevant questions have yet to be answered. What is the effect of the different monomer systems, for example, *i*-PrMgCl and 2-bromo-3-hexyl-5-iodothiophene, as used by the Yokozawa group, in contrast to *t*-BuMgCl and 2,5-dibromo-3-hexylthiophene, as used by McCullough and co-workers? How are the kinetics of the formation of the active Grignard monomer and what is its influence on

Received: January 17, 2011
Revised: March 10, 2011
Published: March 28, 2011

Scheme 1. Active Grignard Monomer Formation via the Two Different Monomer Systems Used in McCullough and Yokozawa Routes and the Proposed Mechanism by McCullough and Yokozawa for the Catalyst Transfer Polymerization



polymerization? Is there an ideal time of polymerization toward good control? Does the quenching reagent methanol affect the end groups and polydispersity of the resulting polymer? How does LiCl influence the polymerization of P3HT?[28]

Here we address these questions and reveal factors that influence the kinetics, leading to clarity regarding end groups and polydispersity. While McCullough and Yokozawa showed that P3HT can be obtained with homogeneous H/Br end groups, we and several other groups often observed a mixture of H/H and H/Br end groups.[18,23,29] Here, we study in detail the parameters causing H/H end groups. We show that one crucial step is the active Grignard monomer formation from the dihalides. Its control is important to obtain homogeneous H/Br end groups, which can be transformed into many functional groups.[29−31] In general, the end group analysis is also seen as a measure of polymerization control and thus often used for mechanistic studies.[27] Therefore, it is essential to know which factors can influence the end groups. Additionally, we present how LiCl—recently used for other polymers—efficiently accelerates the active Grignard monomer formation of P3HT. It also negatively affects the regioregularity and increases the molecular weight of the resultant P3HT polymer. Further, we show that the choice of the right quenching reagent—HCl or methanol—has a major influence on the molecular weight distribution of P3HT. With the help of MALDI-TOF MS, we prove for the first time the formation of coupled polymer chains upon quenching the polymerization with methanol. Thus, general parameters influencing the kinetics of active Grignard monomer formation and catalyst transfer polymerization relevant for any monomer are discussed.

RESULTS AND DISCUSSION

Active Grignard Monomer Formation. In the catalyst transfer polymerization the active Grignard monomer is built *in situ* from the dihalide via a Grignard metathesis reaction. The two main approaches toward this monomer and the mechanism of the polymerization are shown in Scheme 1.[32,33] Generally, the Yokozawa method uses 2-bromo-3-hexyl-5-iodothiophene as a starting material together with *i*-PrMgCl as the Grignard reagent for the metathesis reaction. Because of the higher reactivity of the iodine in comparison to bromine, only one active Grignard monomer **2a** is formed. In contrast, the McCullough method uses 2,5-dibromo-3-hexylthiophene with *t*-BuMgCl as the Grignard reagent. The missing chemical selectivity caused by the two bromine substituents leads to two regioisomers of the active Grignard monomer, **2a** and **2b**. Still the steric hindrance of *t*-BuMgCl along with the 3-alkyl side chain leads to a high amount of the desired isomer **2a** (ca. 75%). The addition of the nickel catalyst Ni(dppp)Cl_2 results in a nickel-inserted dimer **4** with the sterically least hindered tail−tail conformation. Further, according to the proposed mechanisms, the initiating species **5** is built via an intermolecular transfer or an associated pair followed by intramolecular oxidative addition. Now the chain growth proceeds via multiple cycles of transmetalation,

dx.doi.org/10.1021/ma200119s |*Macromolecules* 2011, 44, 3388–3397

Table 1. Overview of Polymers Synthesized Using Different Reaction Conditions[a]

polymer	additive	time for active Grignard monomer [h]	polymerization time [min]	quenching reagent	M_n(SEC) [g/mol]	PDI	H/Br: H/H
P3HT 1		20	165	HCl	4000	1.10	100:0
P3HT 2		2	151	HCl	4000	1.15	30:70
P3HT 3	LiCl	6	22	HCl	6800	1.10	100:0
P3HT 4		2.20	25	HCl	5300	1.14	80:20
P3HT 5	LiCl	6	8	MeOH	6300	1.16	100:0
	LiCl	6	8	HCl	5900	1.10	100:0
P3HT 6		2	110	MeOH	17600	1.28	
P3HT 7		15	2	MeOH	1800	1.30	

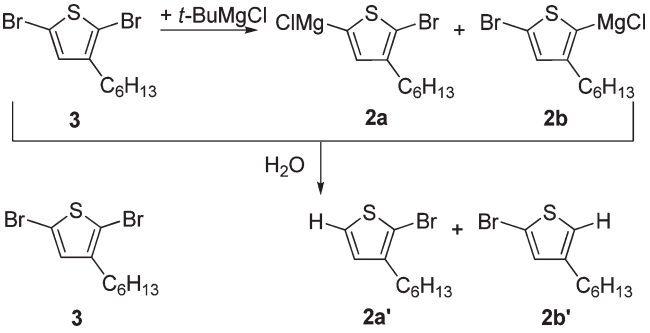
[a] For all P3HTs a monomer **3** to Ni(dppp)Cl_2 catalyst ratio of 26:1 was used except for the P3HT 6 series where the ratio was 89:1. The ratio of monomer to *t*-BuMgCl was maintained at 1:0.96 except for P3HT 2 and P3HT 6 for which the ratio was 1:1. Thus in all cases, an excess of *t*-BuMgCl was avoided.

reductive elimination, and intramolecular oxidative addition. During chain growth, the insertion of the unintended regioisomer **2b** is sterically hindered, and thus it is not consumed during polymerization.[22,32] Therefore, both methods lead to a polymer with a high regioregularity of about 98%, resulting from the insertion of **2a** only.

In one of the first publications about chain growth mechanism, Yokozawa et al. described the ratio of 2-bromo-3-hexyl-5-iodothiophene to *i*-PrMgCl as a critical factor to get low molecular weight distributions and homogeneous H/Br end groups.[33] They recommended 0.95−1 mol equiv of *i*-PrMgCl to 2-bromo-3-hexyl-5-iodothiophene in order to obtain low PDIs and homogeneous H/Br end groups. When we used a similar molar ratio of 1:1 or 1:0.95 for 2,5-dibromo-3-hexylthiophene and *t*-BuMgCl, we still were not able to gain 100% H/Br end groups. Instead, mixtures of H/H and H/Br end groups were obtained for different batches of polymerizations.[23,29] In the literature various procedures were used for the formation of the active Grignard monomer which varied from 1 h at 0 °C[23,33] for the reaction of 2-bromo-3-hexyl-5-iodothiophene with *i*-PrMgCl and 2 h reflux[32] or 2 h at room temperature[34] for the reaction of 2,5-dibromo-3-hexylthiophene with *t*-BuMgCl. Concerning the difference in chemical reactivity of the starting compounds **1** and **3**, fast reactions are expected for 2-bromo-3-hexyl-5-iodothiophene (**1**). However, the time required for the complete formation of the active Grignard monomer, especially for the less reactive 2,5-dibromo-3-hexylthiophene, was uncertain. In the following, the detailed kinetics of active Grignard monomer formation followed by polymerization using Ni(dppp)Cl_2 as catalyst were studied. An overview of the parameters and molecular weights of all polymer samples prepared can be found in Table 1. Several samples were withdrawn during polymerization, and only the molecular weight of the final sample is given here. In the text the first number indicates the polymer batch number and the second number the number of the sample. For example, P3HT 1.15 corresponds to the 15th sample of P3HT 1.

We first investigated the time-dependent formation of the active Grignard species **2a** and **2b** at room temperature from 2,5-dibromo-3-hexylthiophene (**3**) (0.5 M solution in THF) and *t*-BuMgCl (1.23 M solution in THF). The amount of *t*-BuMgCl for all reactions was kept purposefully the same as or a little below (0.96 equiv) that of the dihalide **3** to ensure the complete consumption of *t*-BuMgCl. Room temperature was chosen because earlier reports showed that at higher temperatures the ratio of the two different regioisomers is shifted toward the undesired isomer ((5-bromo-3-hexylthiophen-2-yl)magnesium chloride) **2b**.[32] During the reaction, samples were withdrawn and quenched with H_2O, and the resulting product mixture was analyzed with ^{1}H NMR spectroscopy. All possible quenching products are shown in Scheme 2. After quenching the molecules carry a proton at the position of the respective MgCl group.

Scheme 2. Structures of Possible Products after Quenching the Reaction between 2,5-Dibromo-3-hexylthiophene and *t*-BuMgCl with H_2O



A typical ^{1}H NMR spectrum after 2 h of reaction—a time often used in the literature—is compared to that of the starting compound **3** in Figure 1a. Unreacted 2,5-dibromo-3-hexylthiophene (**3**) has a singlet at 6.78 ppm. In the spectrum of the quenched sample in addition to this signal, two doublets with a coupling constant of 5.6 Hz are observed at 7.18 and 6.79 ppm, which belong to the quenching product of the desired active regioisomer **2a**′. Another doublet for the isomer **2b**′ with a smaller coupling constant of 1.6 Hz is observed at 6.88 ppm. The second doublet of **2b**′ is visible as a small shoulder, and it overlaps with the high field signal of **2a**′. Thus, after 2 h of reaction, the unreacted dibromo compound **3** is still present in the reaction mixture along with the expected active Grignard monomers **2a**′ and **2b**′. The magnified section of the ^{1}H NMR spectra at different reaction times in Figure 1b shows a slow decrease of the singlet corresponding to **3**. Integration of all signals and subtraction of the respective overlapping signals allows for the quantitative determination of all compounds within the accuracy limit of 5% in NMR techniques.

The percentage of each component present at different reaction times is summarized in Table 2. After 2 h, about 34% of the educt **3** is still unreacted. After 20 h, no detectable decrease of the educt peak could be observed. The ratio of the two isomers

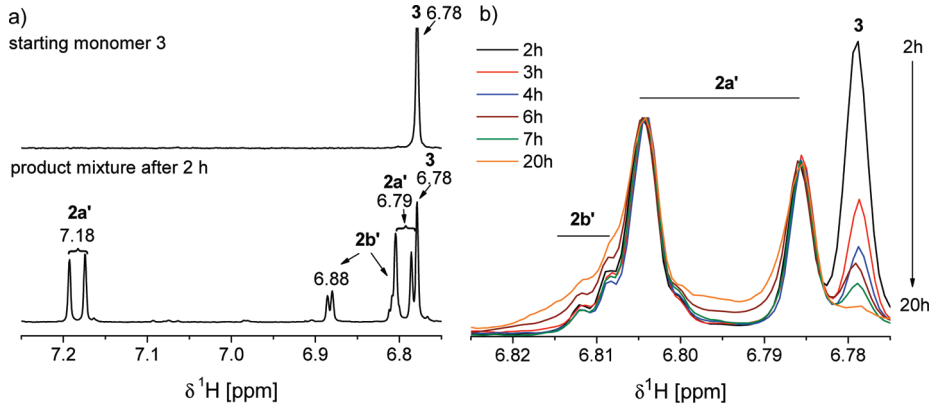


Figure 1. (a) Aromatic region of the ^{1}H NMR spectra of 2,5-dibromo-3-hexylthiophene (**3**) and of a sample quenched with H_2O after 2 h reaction between 2,5-dibromo-3-hexylthiophene and *t*-BuMgCl. The signals are assigned according to Scheme 2. (b) Magnified section of the aromatic region (6.78−6.82 ppm) normalized to the high field doublet of **2a′** at different reaction times. The content of 2,5-dibromo-3-hexylthiophene (**3**) decreases with reaction time continuously up to 20 h.

Table 2. Percentage of Components Present at Different Reaction Times of 2,5-Dibromo-3-hexylthiophene with *t*-BuMgCl at Room Temperature[a]

time [h]	**3** [%]	**2a′** [%]	**2b′** [%]	**2a′:2b′**
2	34	46	20	70:30
3	20	59	21	74:26
4	16	63	22	74:26
6	12	65	23	74:26
7	11	66	23	75:25
20	7	68	25	73:27

[a] The samples were quenched with H_2O, and the components are assigned according to Scheme 2.

2a:**2b** remained nearly constant at about 75:25 for all samples (ranging from 3 to 20 h), and the reaction was very slow. Thus, for the used reaction conditions, almost 20 h is required for the maximum conversion of the dihalide **3** to the active Grignard monomers, **2a** and **2b**.

Since detection of changes in the ^{1}H NMR signal of **3** after 20 h became very difficult and maximum conversion has been achieved, we initiated the polymerization after 20 h. The monomer **3** to Ni(dppp)Cl_2 catalyst ratio was kept at 26:1 to get moderate molecular weights, which allows for proper end group analysis using matrix-assisted laser desorption ionization spectroscopy with time-of-flight detection mass spectroscopy (MALDI-TOF MS). Fifteen samples (P3HT 1.(1−15)) were withdrawn at different stages of the polymerization, quenched with HCl, and analyzed with size exclusion chromatography (SEC) and MALDI-TOF MS. All polymer samples, independent of the polymerization time, had 100% H/Br end groups as observed in the single peak series in MALDI-TOF MS. A representative MALDI-TOF MS spectrum of the final sample P3HT 1.15 (polymerization time: 165 min) with a number-average molecular weight M_n (SEC) of 4000 g/mol and a PDI of 1.10 is presented in Figure 2a. P3HT 1.15 shows the highest peak for the 17-mer with H/Br end groups (Figure 2a). The difference between adjacent peaks corresponds to a 3-hexylthiophene main unit with 166.3 g/mol. To enable a comparison of MALDI-TOF MS spectra at short times of polymerization as well, we selected the 12-mer peak range as a suitable example. These spectra for 14 min (P3HT 1.7), 35 min (P3HT 1.14), and 165 min (P3HT 1.15) of polymerization time are shown in Figure 2b. In all cases, only one signal at 2076 g/mol corresponding to 12-mer with H/Br end groups is seen. A signal for the H/H terminated 12-mer, which would occur at 1997 g/mol, is not visible. Hence, 100% H/Br end groups are formed when a 1:0.96 ratio of 2,5-dibromo-3-hexylthiophene to *t*-BuMgCl is used and a long enough reaction time of 20 h for *in situ* monomer formation, and thus the complete consumption of *t*-BuMgCl is guaranteed. However, the time at which the polymerization was started (here 20 h) is not of general validity for complete conversion of **3**. It can vary depending on the concentration of *t*-BuMgCl. For each experiment, the completion of conversion of **3** must be verified before initiating the polymerization.

Influence of Incomplete Active Grignard Monomer Formation. To study the influence of incomplete *in situ* monomer formation and hence unreacted *t*-BuMgCl, we also initiated a polymerization after 2 h of active Grignard monomer formation. As shown in Table 2, about 34% of the unreacted **3** or an equivalent amount of unreacted *t*-BuMgCl is present in the reaction mixture. The ratio of monomer to Ni catalyst was again kept constant at 26:1. Thirteen samples were withdrawn at different polymerization times, quenched with HCl, and analyzed with SEC and MALDI-TOF MS to get a second series of polymers P3HT 2.(1−13). SEC analysis delivered a final molecular weight of M_n = 4000 g/mol for P3HT 2 similar to that of P3HT 1. One would have expected a lower molecular weight for P3HT 2 compared to P3HT 1, since the available amount of active Grignard reagent **2a** is less for the formation of P3HT 2. But it is possible that other complex reactions may be taking place during the polymerization due to the presence of unreacted dibromide, unreacted Grignard reagent, and MgClBr in the case of P3HT 2, which requires additional studies. While similar molecular weights were reached as in the P3HT 1 series, the end groups were no longer homogeneous and both H/H and H/Br ends groups were obtained. Also, the amount of H/Br end groups in comparison to H/H end groups decreased with the progress of the polymerization. This behavior is visualized in Figure 3 with the MALDI-TOF MS spectra of the final polymer P3HT 1.13 and the ratio of the two peak series for 12 repeating units at different polymerization times of 22, 61, and 151 min. The difference between the two series is 79 g/mol, which is

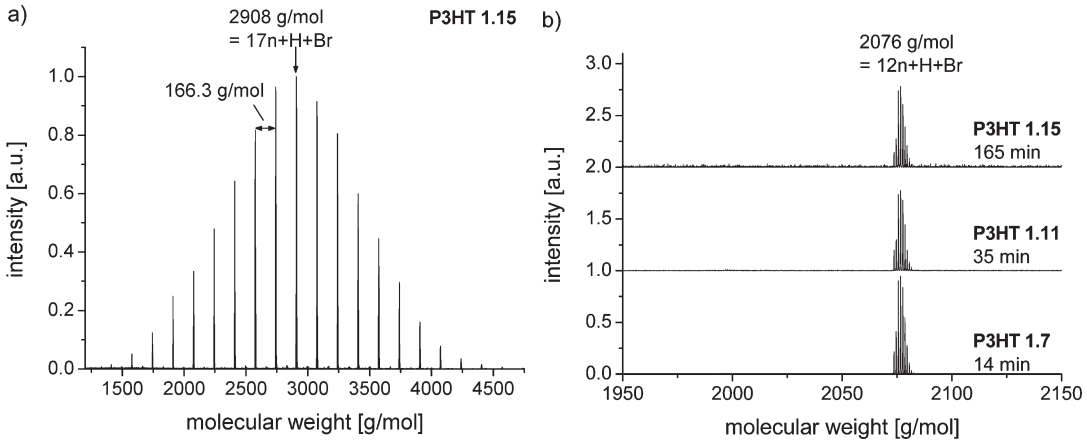


Figure 2. MALDI-TOF MS spectra of (a) P3HT 1.15 obtained after a polymerization time of 165 min, without any unreacted *t*-BuMgCl present during polymerization, and (b) magnified part in the range of 12 repeating units at different polymerization times of 14, 35, and 165 min. Only one series of signals for polymers with H/Br end groups is observed at all polymerization times, and no signal for the 12-mer with H/H end groups is visible at 1997 g/mol.

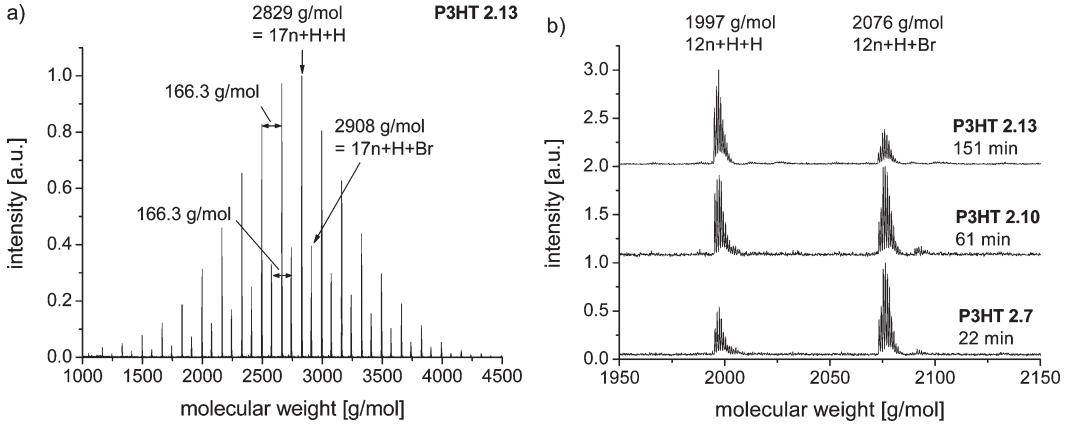


Figure 3. MALDI-TOF MS spectra of (a) P3HT 2.13 obtained after a polymerization time of 151 min with unreacted *t*-BuMgCl present during polymerization and (b) magnified part for 12 repeating units at different polymerization times. Two peak series H/Br and H/H are observed and the intensity of the H/Br end group signal decreases with polymerization time, while the intensity of the undesired H/H signal increases.

consistent with the difference between a bromine and a hydrogen atom.

To show more clearly the time dependence of the amount of H/Br terminated chains, the evolution of the peak molecular weights and the resulting ratios of H/Br to H/H end groups are plotted against polymerization time for both the P3HT 1 and P3HT 2 series in Figure 4. The peak molecular weights were chosen and not the number-average molecular weights to exclude any possible differences caused by different PDIs.

In both cases, the polymerization proceeded quite fast, and after a quick rise of the molecular weight, an almost constant molecular weight was reached after about 20 min. Highly interesting was the development of the end groups during the polymerization. For the P3HT 1 series, where the active Grignard monomer formation was complete and no unreacted *t*-BuMgCl was present, all polymer samples had 100% H/Br end groups independent of the polymerization time. The bromine end originates from the starting unit and the hydrogen end group from quenching the active chain end with hydrochloric acid as shown in Scheme 3 (route 1). On the other hand, in the P3HT 2 series (obtained in the presence of unreacted *t*-BuMgCl) at the early stage of polymerization, the amount of H/Br end groups was high, around 80%. With prolonged polymerization time the amount of H/Br end groups decreased linearly with time, and the undesired H/H end groups became dominating. This can be understood as follows. Incomplete active Grignard monomer formation in the case of the P3HT 2 series causes unreacted *t*-BuMgCl in the polymerization mixture, which can react with the bromine chain end of the polymer to form an active Grignard species (Scheme 3, route 2).[19,35] After quenching with hydrochloric acid, this results in polymer chains with H/H end groups. Since this reaction is rather slow compared to the polymerization, the content of H/Br chain ends is high for short reaction times, during which the chain grows very fast. Thus, short polymerization times are necessary to get a polymer with a high content of H/Br end groups if complete consumption of *t*-BuMgCl during Grignard monomer formation does not take place. For example, we analyzed the end groups of P3HT 2.5, which was quenched after a reaction time of 12 min. The polymer had ~80% H/Br end groups as can be seen in the MALDI-TOF MS spectrum in the Supporting Information. In conclusion, 100% H/Br end groups are only possible when there is no excess of *t*-BuMgCl, which can be realized by the right ratio of 2,5-dibromo-3-

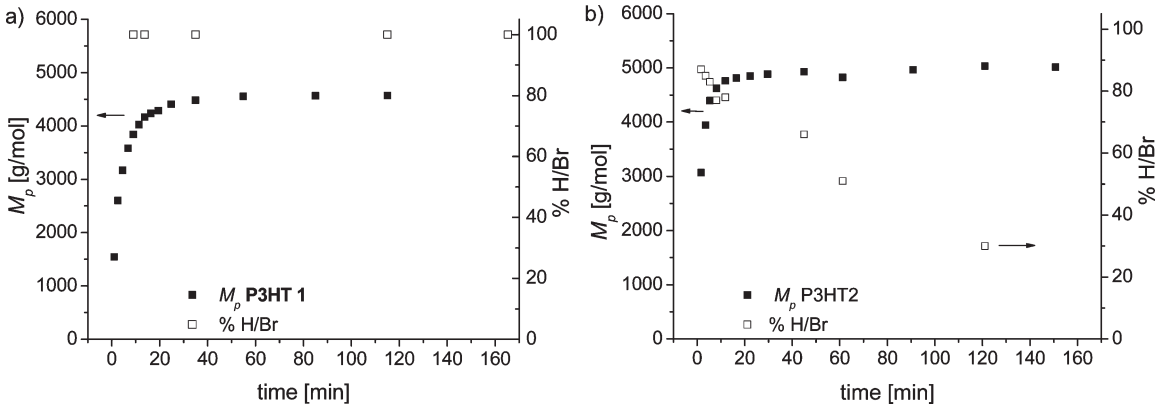
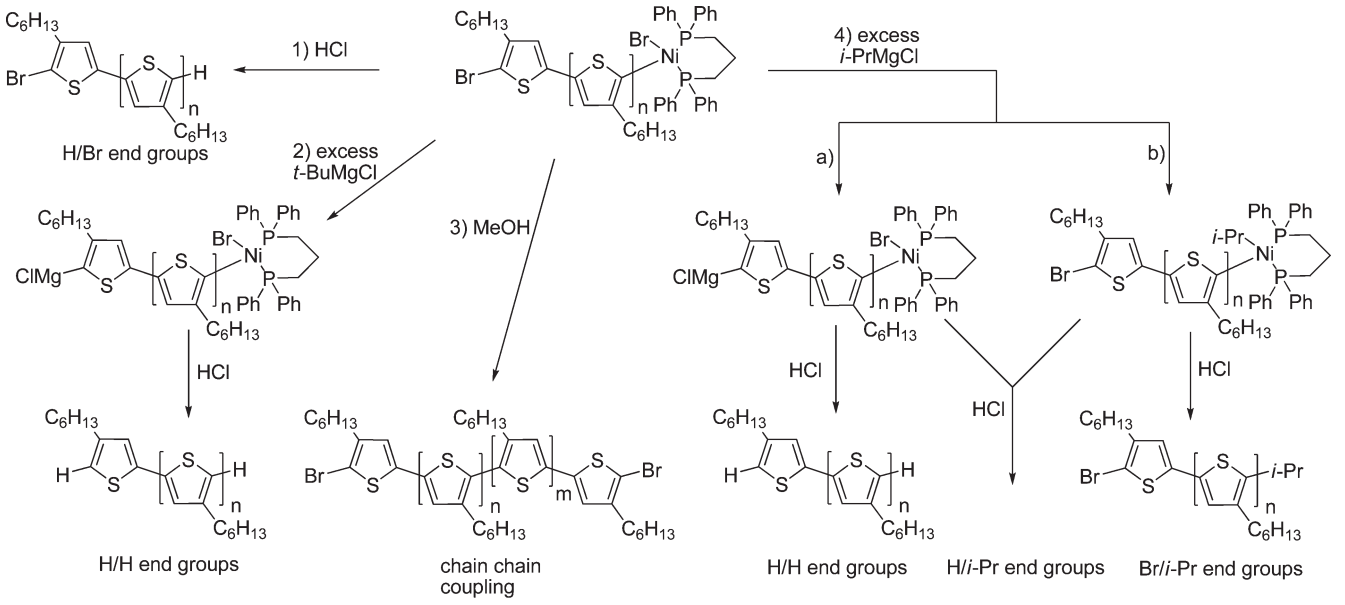


Figure 4. Plot of peak molecular weights M_p and percentage of H/Br chain ends versus polymerization time for (a) P3HT 1.(1−15) without any unreacted *t*-BuMgCl and (b) P3HT 2.(1−13) with incomplete active Grignard monomer formation and thus with an excess of *t*-BuMgCl. With increasing polymerization time, the H/Br content remains constant for P3HT 1, whereas for P3HT 2 the number of H/Br end groups decreases.

Scheme 3. Possible Reactions of the Active Chain End with an Excess of Different Grignard Species and Quenching Reagents[a]



[a] An excess of *t*-BuMgCl affects only the end groups, whereas *i*-PrMgCl can cause both, broader PDI (via end-capping) and undesired H/H or H/*i*-Pr end group formation if present in excess.

hexylthiophene to *t*-BuMgCl and guaranteeing a complete consumption during active Grignard monomer formation. If these prerequisites are not fulfilled, the amount of H/Br end groups will decrease with polymerization time. In the presence of unreacted *t*-BuMgCl, only a maximum of 80% H/Br chain ends can be achieved for short polymerization times. However, since the time for reaching the molecular weight plateau is different for different monomer to catalyst ratios, the quenching time has to be adjusted for each ratio if there is an excess of *t*-BuMgCl in the reaction mixture. Thus, the quintessence of this study is that 100% H/Br end groups for any desired molecular weight can be obtained by guaranteeing no unreacted *t*-BuMgCl in the polymerization mixture.

The next question was the influence of excess or unreacted *t*-BuMgCl on the PDI of the resulting P3HT. Therefore, the PDI of both series of P3HT 1.(1−15) and P3HT 2.(1−13) are plotted against polymerization time in Figure 5.

The polydispersity of both polymers was low between 1.09 and 1.15. The final samples, P3HT 1.15 and P3HT 2.13, had a polydispersity of 1.1 and 1.15, respectively. Thus, there is no noticeable effect of unreacted *t*-BuMgCl on the PDI. Usually end-capping reactions can cause an increase in PDI. However, because the steric demand of *t*-BuMgCl is high, end-capping reactions do not occur, and so a low PDI is maintained. McCullough et al. showed that when *t*-BuMgCl was used as a potential end-capping reagent, no chains with a *t*-Bu end group were formed.[36] Thus, the steric hindrance of the tertiary Grignard reagent is too high for this reaction with the active chain end and does not abort the chain growth or cause a broader PDI.

The difference in the steric demand of the Grignard reagents *i*-PrMgCl and *t*-BuMgCl is also one important factor when the monomer routes of McCullough and Yokozawa are compared. Yokozawa et al. showed that already a 1.2 M excess of *i*-PrMgCl

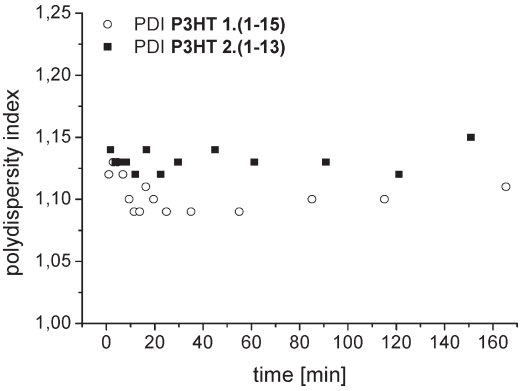


Figure 5. Polydispersity index (PDI) of P3HT 1.(1−15) and P3HT 2.(1−13) versus polymerization time. The PDIs of both polymer series are low, and that of P3HT 2.(1−13) was also not significantly affected by unreacted *t*-BuMgCl.

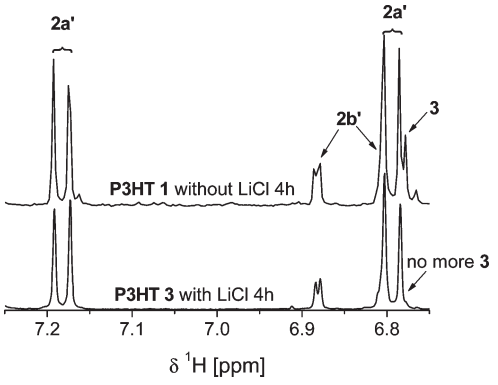


Figure 6. Aromatic region of the ^{1}H NMR spectra of samples quenched with H_2O after 4 h reaction for the expected active Grignard monomers between 2,5-dibromo-3-hexylthiophene (**3**) and *t*-BuMgCl with and without LiCl. For P3HT 3 with LiCl as an additive no signal for **3** is observed, which shows the completion of the reaction in 4 h.

does not only affect the end groups, but also the molecular weight distribution of P3HT.[33] Recently, it was shown that by using *i*-PrMgCl as Grignard reagent for the polymerization of P3HT and poly(9,9-dioctylfluorene), the resulting polymers had small amounts of *i*-Pr end groups.[16,33] This indicates that *i*-PrMgCl can at least partly react with the active chain end and thus cause dead ends and a broad polydispersity (Scheme 3, route 4). On the other hand, an excess of *t*-BuMgCl does not influence the PDI but causes a loss of Br end groups, depending on the time of polymerization. Thus, the observed major differences for the two different monomer systems depend on the steric demand of the Grignard reagents.

Influence of LiCl as an Additive. As shown above, a complete consumption of *t*-BuMgCl is essential to get homogeneous H/Br end groups. However, this is difficult to realize at room temperature. Continuous monitoring of the reaction is necessary, and the reaction times are very long, varying between 20 and 30 h. Increasing the temperature would be an alternative, but McCullough et al. showed that it also influences the ratio of the two active Grignard isomers. More and more of the undesired active monomer **2b** (whose incorporation decreases the regioregularity of the polymers) is formed at higher temperatures.[32] Recently, LiCl was used as an additive for the polymerization of different polymers such as poly(*p*-(2,5-bishexyloxy)phenylene), poly(9,9-dioctylfluorene), poly(*N*-dodecylpyrrole), and P3HT with *i*-PrMgCl as the Grignard reagent.[14,16,22,28] Knochel et al. showed that LiCl can significantly accelerate the Br/Mg exchange between a Grignard reagent and aryl halides. It also increases the total yield of the metathesis reaction.[37,38] LiCl breaks up Grignard aggregates through the formation of a Grignard−LiCl complex with a strong magnesiate character ($RMgCl_2^-Li^+$). This is discussed as the origin of the high reactivity of these complexes.

Therefore, we studied (i) if LiCl can also be used as an additive in conjunction with *t*-BuMgCl and 2,5-dibromo-3-hexylthiophene to accelerate the active Grignard monomer formation and (ii) the influence of LiCl on the end groups and the PDI. We reacted 2,5-dibromo-3-hexylthiophene, LiCl, and *t*-BuMgCl at a molar ratio of 1:1:0.96. The influence of the LiCl on the rate of formation of the active Grignard monomer was very strong. Already after 4 h the dibromide **3** was consumed completely, as shown in Figure 6. In contrast to activation by temperature, the acceleration using LiCl did not negatively affect the ratio of the two regioisomers **2a**:**2b**. The ratio obtained was 78:22. Without adding LiCl at room temperature it was about 74:26.

For the polymerization the ratio of monomer to Ni catalyst was kept at 26:1 as in the former experiments. Ten samples were withdrawn at different times, quenched with HCl, and analyzed with SEC and MALDI-TOF MS to get a third series of polymers P3HT 3.(1−10). The resulting polymer P3HT 3.10 (after 22 min of polymerization) had 100% H/Br end groups (for MALDI-TOF MS see Supporting Information) as expected because of the complete consumption of *t*-BuMgCl. Unexpected was the influence of LiCl on the molecular weight and the regioregularity of the polymer. In Figure 7 the peak molecular weights M_p of P3HT 1 series and P3HT 3 series are plotted against the polymerization time. In both series no unreacted *t*-BuMgCl was present during the polymerization. Only the data for the first 30 min are shown here, since a plateau was already reached in both cases.

For the P3HT 3 series with LiCl as an additive, the final molecular weight plateau is reached after the same polymerization time (∼15−20 min) as for the P3HT 1 series. However, the resulting molecular weight is higher for the P3HT 3 series. The final sample P3HT 3.10 (22 min of polymerization time) has a number-average molecular weight of 6800 g/mol, whereas the molecular weight for P3HT 1.15 (2 h of polymerization time) was 4000 g/mol. SEC molecular weights of P3HT are usually overestimated because of the chain stiffness of P3HT in comparison to the polystyrene calibration standards. Thus, the more reliable repeating units are calculated from MALDI-TOF MS. For P3HT 1.15 the M_n(MALDI) was 3000 g/mol, corresponding to 18 repeating units and for P3HT 3.10 3700 g/mol, corresponding to 22 repeating units. This was unexpected since the same monomer-to-catalyst ratio was used for both P3HTs. The effect of LiCl on the molecular weight was much higher than any expected experimental error possible during the polymerization procedure. This difference in molecular weight was reproducible for different batches and for different monomer-to-catalyst ratios.

The increase in molecular weight caused by LiCl can be either due to an increase in polymerization rate or due to incorporation of the second isomer **2b** or both. To distinguish between these effects, the normalized peak molecular weights (obtained by dividing by the maximum molecular weight) are plotted in Figure 7b. To quantify the difference in rate of polymerization, we measured the slope in the linear range of both curves. We

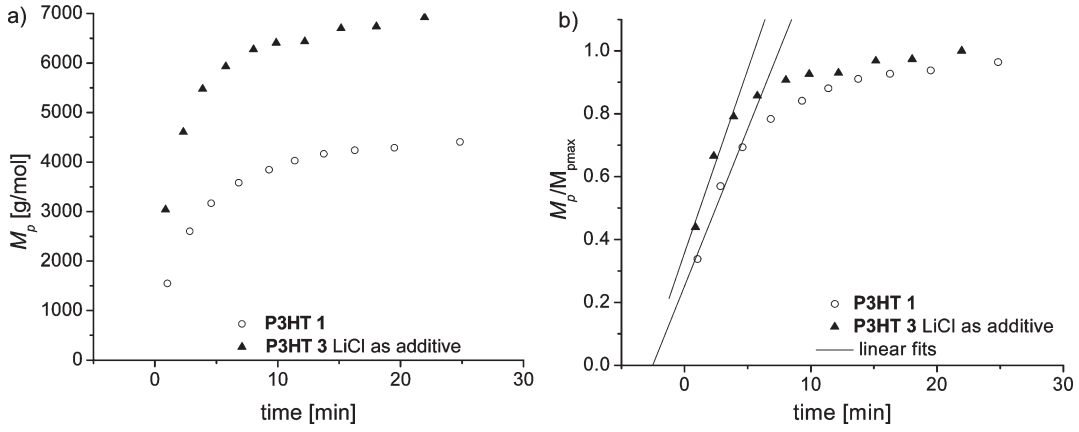


Figure 7. Plot of (a) peak molecular weights M_p and (b) M_p/M_{pmax} versus polymerization time for the P3HT 1 series without and the P3HT 3 series with LiCl as an additive. For both polymers no unreacted *t*-BuMgCl was present in the polymerization mixture, and a monomer-to-catalyst ratio of 26:1 was used. In (b) the straight lines indicate fits for the linear range.

observed a 17% increase in rate by using LiCl. Thus, this is the main cause for the increase in molecular weight. Further we studied if **2b** is incorporated, which should negatively affect the regioregularity of P3HT and irregular couplings should be visible in ^{1}H NMR. Indeed, the polymers obtained with LiCl as an additive showed a small amount of irregular couplings at 7.02 (HT-HH; H = head; T = tail) and 7.05 ppm (TT-HH) (see Supporting Information). In contrast, for P3HTs polymerized without LiCl no irregular couplings could be observed. An estimation of the quantitative change in regioregularity is not possible because it lies within the 5% accuracy limit of ^{1}H NMR. For qualitative information, the aromatic regions of relevance for the regioregularity in ^{1}H NMR are shown in the Supporting Information for two different molecular weights. Thus, LiCl increases the rate of polymerization considerably and facilitates the incorporation of the undesired monomer **2b** to a small extent.

The effect of even small changes of the regioregularity on the charge carrier mobility and the performance of organic solar cells has often been discussed in the literature.[39−42] Thus, we measured OFETs to see whether the charge carrier mobility is affected by this small change in regioregularity. To eliminate differences in mobility caused by differences in molecular weight, two polymers with similar number-average molecular weights—one without LiCl (P3HT 4 M_n = 5300 g/mol) and one with LiCl as an additive (P3HT 5 M_n = 5900 g/mol)—were synthesized and compared as representative examples. Both polymers show the same charge carrier mobility (μ_{sat}) of 2×10^{-3} cm^2/(V s). Thus, the effect of the small decrease in regioregularity caused by the use of LiCl on the charge carrier mobility is negligible. Therefore, LiCl is a very helpful additive for efficient acceleration of the active Grignard formation and rate of polymerization. It increases the molecular weight without changing the monomer to catalyst ratio and allows for the easy access of 100% H/Br end groups.

Influence of Quenching Reagent on Polydispersity. Apart from the active Grignard monomer formation, there are other factors such as quenching agents which strongly influence the polymerization of P3HT. Rawlins et al. reported that there is no effect on the polydispersity when methanol is used as a quenching agent instead of hydrochloric acid.[43] In contrast to their findings, we see a clear increase in the polydispersity via coupling when using methanol as a quenching reagent. Therefore, we studied in detail the influence of quenching agents on chain−chain coupling. We compared P3HT 5 (obtained by adding LiCl) and P3HT 6 (without LiCl) and analyzed the effect of the quenching reagents, methanol or HCl, on the resulting polymers (Figure 8). During the polymerization of P3HT 5, two samples were taken after 8 min and quenched with either HCl or methanol. The SEC curves of the respective samples of P3HT 5 are presented in Figure 8a. The sample with methanol as a quenching reagent shows an undesired shoulder exactly at double the molecular weight, while the sample quenched with hydrochloric acid has a monomodal distribution. Thus, the origin for the chain−chain coupling could only be the quenching reagent, which increases the polydispersity from 1.10 to 1.16. This is supported by the fact that all polymers synthesized without adding LiCl and quenched with HCl also showed a monomodal distribution. The SEC curve of P3HT 1.15 is shown as a representative example in Figure 8b. Further, during polymerization of P3HT 6 (without LiCl as additive) seven samples were withdrawn and quenched with MeOH and analyzed with SEC. It can be clearly seen that the amount of chain−chain coupling depends on the molecular weight as depicted in Figure 8b. This can be understood as follows. With increasing molecular weight it is less likely for two active chain ends to meet and react. This causes a decreasing amount of coupling. The fact that P3HT 5 was polymerized with LiCl as an additive and P3HT 6 without it shows that MeOH and not LiCl is the reason for chain−chain coupling.

These findings are in agreement with the observation of Yokozawa et al. when they used water as quenching reagent instead of hydrochloric acid.[44] They proposed that the slow quenching with water can result in disproportionation of the NiL_2 group at the active chain end, leading to coupled chains. This results in a bimodal molecular weight distribution and a higher polydispersity. To verify this, the end groups of P3HT 5 were analyzed with MALDI-TOF MS. Accordingly, a low molecular weight peak series with H/Br end groups and a high molecular peak series with Br/Br end groups are expected. This is because disproportionation of active Ni chain ends would lead to polymers with two bromine end groups at double the molecular weight. Unfortunately, only the low molecular weight series could be detected in MALDI-TOF MS (see Supporting Information). The reason is that it is difficult to observe the minor component of coupled chains at higher molecular weights because of the broad

dx.doi.org/10.1021/ma200119s |*Macromolecules* 2011, 44, 3388–3397

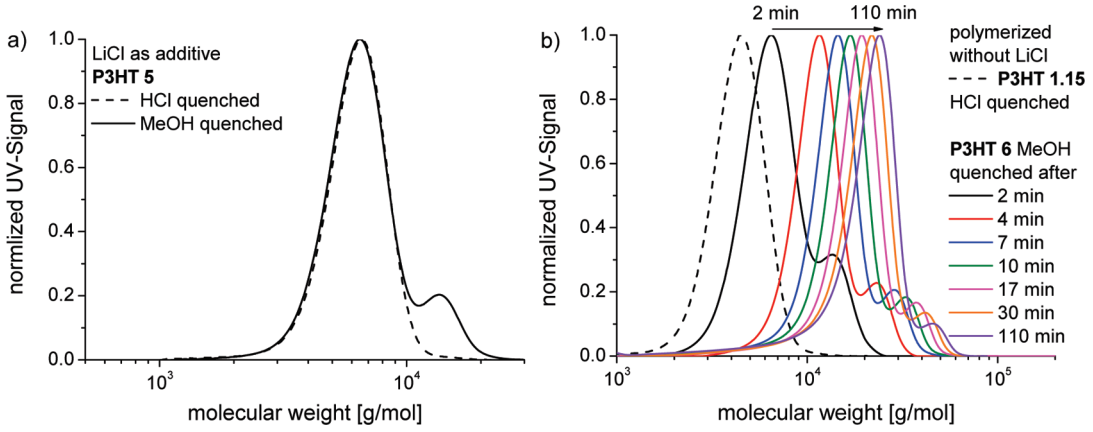


Figure 8. (a) SEC curves of samples of P3HT 5 (polymerized with LiCl as an additive) taken after 8 min and quenched with either methanol or with hydrochloric acid. (b) SEC curves of samples of P3HT 6.(1−7) taken at different polymerization times and quenched with methanol together with P3HT 1.15 quenched with HCl. With increasing molecular weight of P3HT 6.(1−7), the amount of coupled chains decreases.

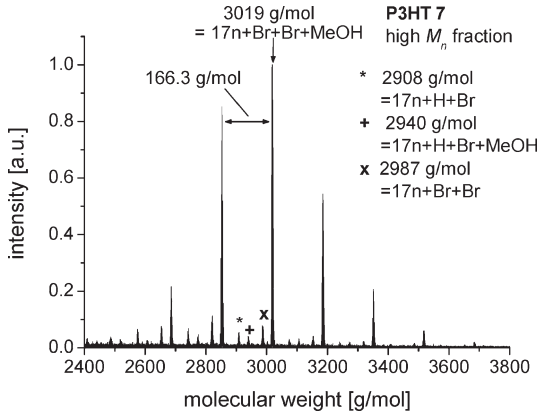


Figure 9. MALDI-TOF MS spectrum of the coupled chain fraction of P3HT 7, which was obtained by preparative SEC. One main peak series for P3HT with two bromine end groups and one MeOH unit is observed. Minor peaks are explained in the legend.

distribution and due to the better tendency of the low molecular weight series to ionize into the gas phase. Therefore, we used preparative SEC to separate the two fractions and additionally used a sample with very low molecular weight (P3HT 7) to observe the coupled chains (see Supporting Information for SEC). A MALDI-TOF MS spectrum of the high molecular weight fraction containing the coupled chains is shown in Figure 9. One major peak series is observed which corresponds to P3HT with two bromine end groups and one methanol unit (3019 g/mol = 17 × 166.3 g/mol + 2 × 79.9 g/mol + 32 g/mol). The fact that two bromine groups are present in one polymer chain proves the disproportionation. Thus, the origin of the high molecular weight fraction during quenching with methanol is elucidated as chain−chain coupling for the first time. However, the mechanism of incorporation of the MeOH molecule remains unclear. Negligible peaks seen in Figure 9 belong to P3HT with H/Br, H/Br + MeOH, and Br/Br chain ends.

CONCLUSION

We have shown that a complete active Grignard monomer formation and thus an entire consumption of *t*-BuMgCl are crucial to get polymer chains with 100% H/Br end groups. If this is not guaranteed, the amount of H/Br end groups will decrease with polymerization time. The full monomer conversion requires long reaction times when *t*-BuMgCl and 2,5-dibromo-3-hexylthiophene are used at room temperature. This leads to tedious control via ^{1}H NMR to ensure the completion of the reaction. To overcome these problems, we used LiCl as an additive to effectively accelerate the active monomer formation. Furthermore, adding LiCl leads to an increase in molecular weight without changing the monomer-to-catalyst ratio. The origin of this effect is due to both an increase in rate of polymerization and the incorporation of small amounts of the undesired isomer **2b**, which causes a slight decrease of the regioregularity. This did not negatively affect the charge carrier mobility of P3HT. Additionally, we demonstrated that methanol as a quenching reagent causes chain−chain coupling via disproportionation. The amount of coupling decreased with increasing molecular weight. With the importance of the right quenching reagent and the role of unreacted *t*-BuMgCl, we identified all the factors relevant for catalyst transfer polymerization toward perfect end group control and low PDIs. This will lead to a better understanding of the chain growth polymerization and its use for complex polymer architectures in combination with other polymerization techniques.

ASSOCIATED CONTENT

Supporting Information. Experimental details, MALDI-TOF MS spectra, ^{1}H NMR spectra, SEC curves, and output characteristics of OFETs. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

R. H. Lohwasser thanks the Universität Bayern e.V. for a research stipend according to the Bayerisches Eliteförderungsgesetz. We also acknowledge DFG (SPP1355 and SFB 840) for financial support.

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NOTE ADDED AFTER ASAP PUBLICATION

This article posted ASAP on March 28, 2011. Figure 9 has been revised. The correct version posted on April 5, 2011.