7638 *Macromolecules* **2009**, *42*, 7638–7641
DOI: 10.1021/ma901888h

Macromolecules
COMMUNICATION TO THE EDITOR

Incorporation of Different End Groups in Conjugated Polymers Using Functional Nickel Initiators

Alfons Smeets,[†] Karlien Van den Bergh,[†] Julien De Winter,[‡] Pascal Gerbaux,[‡] Thierry Verbiest,[†] and Guy Koeckelberghs*,[†]

[†]*Laboratory of Molecular Electronics and Photonics, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium, and* [‡]*Mass Spectrometry Center, Organic Chemistry Laboratory, University of Mons, 20 Place du Parc, B-7000 Mons, Belgium*

Received August 25, 2009
Revised Manuscript Received September 24, 2009

Well-defined conjugated polymers remain intensively studied polymers, since they reveal promising applications in the field of molecular electronics.[1] These polymers significantly owe their potential to the fact that their polymerization can proceed via a chain-growth mechanism, as demonstrated by McCullough et al.[2,3] and Yokozawa et al.[4,5] They showed that the polymerization of monobromo-monobromomagnesio-3-alkylthiophenes to head-to-tail poly(3-alkylthiophene)s (HT-P3ATs) proceeds via a controlled chain-growth mechanism in the presence of Ni(dppp)Cl_2 (dppp = 1,3-bis(diphenylphosphino)propane). This also allows the synthesis of HT-P3ATs end-capped with selected functional groups,[6−8] which may act (after some transformations) as an initiator for the polymerization of a second block, for instance poly(styrene) or poly(methyl acrylate).[9] Second, the living nature of the polymerization allows the preparation of conjugated block copolymers by successive additions of the respective monomers.[10−16]

Apart from HT-P3ATs, other conjugated polymers have also been prepared in a chain-growth mechanism using Ni[17] and Pd[18,19] catalysts, and the quasi-controlled nature of their polymerizations was demonstrated. Nevertheless, the presence of Br-terminated polymer chains[4] indicated that not all of the polymer chains are living (vide infra) during the polymerization. This complicates the end-capping process of these polymers, given the fact that some chains will not react. Applied to the formation of block copolymers, this will result in a mixture of the desired block copolymer and homopolymers of the first block. Moreover, the synthesis of block copolymers by successive additions of the different monomers also requires that the polymerization of both polymer blocks proceeds under the same reaction conditions and using the same catalyst. Unfortunately, this is not always the case, which complicates the preparation of these polymer materials.[10,11]

In contrast, if such chain-growth polymerizations would be initiated by a functionalized Ni catalyst, all chains would bear the functional group (at the beginning of each chain), regardless of whether the polymerization is perfectly controlled or not. This would allow the synthesis of a broad variety of conjugated polymers equipped with a functional group. Moreover, if the polymerization proceeds in a controlled way, polymers equipped with two different functional groups at both ends can be prepared. This Communication reports the synthesis of functionalized Ni catalysts and their use for the synthesis of conjugated polymers end-capped with these functional groups.

When HT-P3ATs are synthesized using Ni(dppp)Cl_2, the first step constitutes a nucleophilic attack of the monomer (**1**) on Ni(dppp)Cl_2, yielding **2** (Scheme 1).[4] Propagation consists of a second nucleophilic attack on Ni, subsequent transmetalation, and oxidative insertion into the terminal C−Br bond. Importantly, the Ni catalyst is not released from the polymer chain. Instead, it remains complexated to the conjugated system, moving to the terminal C−Br bond via a ring walking process,[20] and therefore, it exclusively reacts intramolecularly. As a consequence, in a living polymerization, all chains must be H/Br end-capped after termination with acid. Indeed, the Br atom is present at the beginning of each polymer chain, whereas the hydrogen atom originates from the replacement of the Ni center by H. If the polymerization proceeds in an uncontrolled manner, this is manifested by the nature of the end groups. If, for instance, the oxidative insertion of the Ni catalyst fails, which terminates the polymerization at that particular chain, the polymer chain would be Br/Br end-capped. If, on the other hand, two growing polymer chains disproportionate, also two Br end groups would be present. H/H, finally, can be formed by reaction of (excess) Grignard reagents in a metathesis reaction.[21]

It is clear that **2**, prepared in situ, is in fact the real initiator. On the other hand, the required organometallic species can be prepared in a separate step and added as initiator. For instance, phenyl-functionalized Ni[20,22] and Pd catalysts[23] have been used to initiate the polymerization of HT-P3ATs and poly(fluorene)s, respectively. The purity and stability of the externally prepared initiator are of crucial importance, since traces of any Ni^{2+} salt result in polymer chains that are not initiated by the initiator and therefore lack the functional group. Alternatively, Doubina et al. reported a one-pot protocol in which phenyl-functionalized Ni initiators were prepared in situ and used as initiators for HT-P3HT.[24] Although it shows some practical advantages, it also produces significant amounts of polymer chains lacking the initiating group, probably due to the presence of some Ni impurities.

First, **3a** (Scheme 2) was prepared in order to investigate the feasibility of isolating a stable nickel−aryl initiator. The synthesis of **3a** was accomplished through addition of phenyl bromide to $Ni(PPh_3)_4$.[25] No chelating phosphine was added, as reported by Bronstein et al.,[22] since the polymerization of different monomers often requires the use of differently ligated catalysts, which might in this case easily be accomplished by the addition of the respective ligands to the parent bis(triphenylphosphino)nickel initiator (vide infra). Although perfectly air-stable, as reported previously,[26] **3a** appeared to be very unstable in solution in our hands. Indeed, after a few minutes, the solution is discolored and a white precipitate is formed. The decomposition appears to proceed quite rapidly, which complicates the isolation of this complex. If **3a** is allowed to fully decompose and the end products are analyzed, triphenylphosphine and biphenyl could be recovered. This suggests that the Ni initiator disproportionates (eq 1). In this process, Ni^{2+} salts are also formed, which can initiate the polymerization, resulting in polymer chains without a phenyl group.

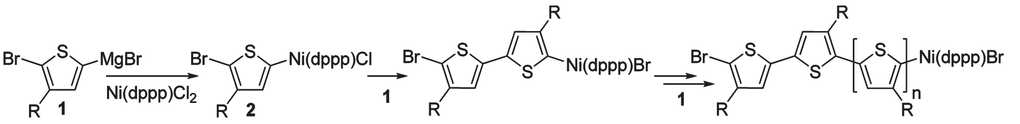
$$2PhNi(PPh_3)_2Br \rightarrow Ni + 2PPh_3 + Ph-Ph + Ni(PPh_3)_2Br_2 \tag{1}$$

This disproportionation can, however, be suppressed if an *o*-tolyl instead of a phenyl group is employed. In that case,

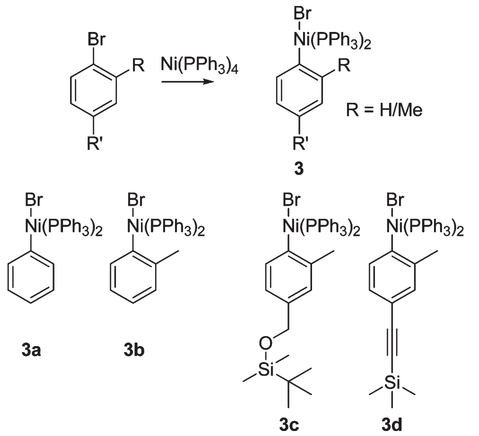
---

*Corresponding author. E-mail: guy.koeckelberghs@chem.kuleuven.be.

Scheme 1. Catalyst-Transfer Mechanism of Poly(3-alkylthiophene)s (R = Alkyl, dppp = 1,3-Bis(diphenylphosphino)propane)



Scheme 2. Synthesis and Structure of the Ni Initiators



2,2′-dimethyl-1,1′-biphenyl should be the end product, corresponding to the formation of HH couplings, which are only very slowly produced from Ni complexes.[27−29] The required catalyst **3b** has already been used by Kiriy et al. for the study of the polymerization of P3ATs and as mimics for surface-immobilized initiators.[25,30,31] Indeed, **3b** shows a significantly increased solution stability, and after 1 h—the typical duration of a polymerization and much longer than the initiation—no precipitate is formed, and the ^{1}H NMR spectra before and after (Supporting Information) this period were identical. All $Ni(PPh_3)_2$ complexes were prepared by an oxidative addition of the corresponding phenyl bromides to freshly prepared $Ni[PPh_3]_4$.

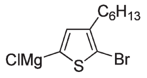
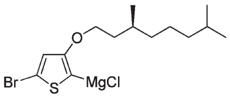
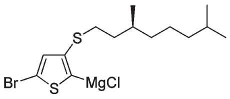
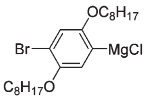
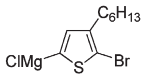
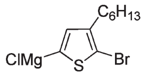
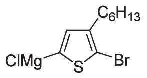
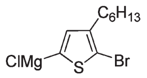
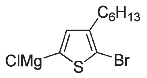
Next, we investigated whether **3b** can be used to initiate the polymerization of a broad range of conjugated monomers (alkyl-,[4] alkoxy-,[32] and thioalkyl-substituted[33] thiophenes and dialkoxybenzenes;[34] Table 1, entries 1−4). In all cases, polymers were recovered, and the ^{1}H NMR spectra (Supporting Information) revealed the incorporation of the initiator moiety. As can be derived from the MALDI-ToF (matrix-assisted laser desorption ionization−time-of-flight) spectra (Supporting Information) and summarized in Table 1, the polymer chains were mostly equipped with an *o*-tolyl end group, demonstrating that **3b** was the dominant initiator and that little or no other initiators, which would result in Br/Br, Br/H and H/H end-cappings, such as Ni^{2+} salts, were introduced or formed in situ during the polymerization. No *o*-Tol/*o*-Tol end groups were found for P3AT, which demonstrates that disproportionation of the growing P3AT chains did not occur. Again, this is consistent with the fact that the formation of HH couplings is not promoted by the Ni catalyst for 3-alkylthiophenes.[28] In the case of poly(3-alkoxythiophene) (P3AOT) and poly(3-alkylthiothiophene) (P3ATT), for which we showed that HH couplings can be formed using Ni catalysts[32,33,35] and that this disproportionation is therefore possible, some traces of *o*-Tol/*o*-Tol end groups are found. Finally, the presence of *o*-Tol/Br and Br/Br end groups indicates that termination reactions occurred, originating from an imperfect intramolecular migration and subsequent oxidative insertion of the Ni catalyst. We therefore conclude that the protocol is applicable for the initiation of a variety of conjugated monomers but that termination reactions and, depending on the nature of the substituent, some disproportionation also occur.

On the other hand, the polymerization of **1** in the presence of $Ni(dppp)Cl_2$ is known to proceed in a controlled way, exclusively resulting in Br/H end groups.[21] As a consequence, the presence of *o*-Tol/Br end groups in the polymerization of **1** when initiated by **3b** reveals that $Ni[PPh_3]_2$ dissociates from the growing polymer chain, terminating the polymerization. It has been shown[10] that a proper choice of the ligand plays a crucial role in a successful Ni-catalyzed polymerization of conjugated monomers and that the chloro(2-tolyl)(dppp)nickel-initiated polymerization of poly-(3-hexylthiophene) is living.[22] Therefore, the polymerization of **1** was also performed in the presence of 1 and 2 equiv of dppp (Table 1, entries 5 and 6). The additional dppp was added to **3b** before **1** was cannulated to the mixture in order to allow ligand exchange before the polymerization actually starts. In this respect, the solubility of the Ni complex significantly increases in the presence of dppp, suggesting that ligand exchange occurs. The decrease and eventual disappearance of *o*-Tol/Br end groups in the MALDI-ToF spectra of the polymers (Supporting Information) confirms that the termination reaction can indeed be suppressed, which agrees with the results of Bronstein et al., who performed the ligand exchange before the isolation of the nickel initiator.[22] Apart from a minor (< 5%) fraction of polymer chains that were not initiated by **3b**, the polymerization and initiation were under control. Hence, it should be possible to polymerize different conjugated monomers using the optimal ligand for their respective polymerizations starting from the parent bis(triphenylphosphino)nickel initiator.

In a next series of experiments, Ni initiators equipped with a functional group (**3c**,**d**) were prepared and used to initiate the polymerization of **1**. Again, 2 equiv of dppp were added to suppress termination reactions. The ^{1}H NMR spectra revealed the incorporation of the functional groups, without any degradation or deprotection. The MALDI-ToF spectra (Supporting Information) show that, apart from a minor amount of wrongly initiated polymer chains, the polymerization initiated by **3c** proceeded analogous to that initiated by **3b** with added dppp.[36] In contrast, for **3d** some termination reactions again occurred, which may be attributed to the complexation of the Ni moiety with the acetylene group.[37−39] A similar behavior has previously been observed in the end-capping reaction of P3ATs with acetylenic moieties.[7] These results demonstrate that the use of Ni−phenyl initiators bearing a methyl group in the *ortho*- and a functional group in the *para*-position are able to introduce a broad variety of functional groups into conjugated polymers.

Finally, the controlled nature of the polymerization of **1** using functional Ni initiators was exploited to prepare a P3HT which is end-capped with two different functional groups. Such polymers are particularly useful for the synthesis of triblock copolymers composed of three different (conjugated) blocks. Therefore, **1** was initiated by **3b** in the presence of 2 equiv of dppp, and the polymerization was quenched by the addition of 4-chloromagnesioanisol, which should result in a polymer end-capped with *o*-Tol/*p*-anisol end groups. Both MALDI-ToF and ^{1}H NMR analysis showed that this is indeed the case for the majority of polymer chains. However, not all *o*-Tol end-capped chains also bear a *p*-anisol moiety on the other end. This incomplete conversion could possibly be attributed to the nature of the employed Grignard reagent. Also, a very small amount of polymer chains without *o*-Tol end groups were observed. This is visualized by the presence of H/H, H/*p*-anisol, and *p*-anisol/*p*-anisol terminated

Table 1. Overview and Results of the Polymerizations Performed

entry	monomer[a]	initiator	ligand added	$\overline{M}_n$ (kg/mol)[b] GPC[c] ^{1}H NMR[d] MALDI-ToF	end-groups[e]			
					In[f]/H	In/Br	Br/Br + Br/H + H/H	In/In
P1		**3b**	/	3.0 (1.3) 1.7 1.8	65%	15%	20%	0%
P2		**3b**	/	5.5 (1.9) n/a 1.7	40%	45%	15%	~0%
P3		**3b**	/	1.8 (1.3) n/a 1.8	40%	60%	0%	traces
P4		**3b**	1 eq dppe[g]	3.5 (1.2) n/a 2.5	[h]	[h]	[h]	0%
P5		**3b**	1 eq dppp[i]	3.8 (1.5) 1.4 1.7	85%	5%	10%	0%
P6		**3b**	2 eq dppp	2.6 (1.2) 1.8 1.7	95%	0%	5%	0%
P7		**3c**	2 eq dppp	3.7 (1.3) 2.2 1.9	95%	0%	5%	0%
P8		**3d**	2 eq dppp	3.2 (1.3) 2.1 1.9	80%	10%	10%	0%
P9		**3b**	2 eq dppp	2.0 (1.2) n/a 1.8	n/a	n/a	n/a	n/a

[a] The monomer formation was checked by ^{1}H NMR spectroscopy and found to be quantitative for **P1** and **P5**−**P9**, 31% for **P2**, 64% for **P3**, and 78% for **P4**. [b] Of the samples after washing with acetone. [c] In THF toward poly(styrene) standards. The polydispersities are given in parentheses. GPC tends to give erroneous results for, for instance, P3AOTs, putting the results of **P2** (and **P3**) into perspective. [d] Determined from the mean of the ratios of the integrals at 2.8 ppm/2.4 ppm and 7.0 ppm/6.9 ppm. [e] Determined by MALDI-ToF. [f] In = initiator. [g] dppe = 1,2-bis(diphenylphosphino)ethane. [h] The MALDI-ToF spectra indicate that two sets of polymer chains are present, Tol/X and Br/X end-capped in a 10/3 ratio, with X unknown, corresponding to a mass of 82 Da and different from Tol and Br. This shows that no disproportionation occurs, that ~80% of the chains are initiated by the Ni initiator, but that an unknown termination reaction occurs. [i] dppp = 1,3-bis(diphenylphosphino)propane.

polymer chains—the latter two arising from reaction of 4-chloromagnesioanisol with a polymer chain not initiated by *o*-tolyl, in which case both mono- and dicappings are likely to take place.[8]

In conclusion, we have demonstrated that functionalized Ni−phenyl initiators, provided they possess an *o*-methyl group for stability reasons, can be prepared and used to initiate the polymerization of several conjugated polymers. This concept should therefore be applicable to a wide variety of conjugated monomers which can be polymerized using a Kumada catalyst-transfer mechanism. Substitution of the phenyl moiety allows the insertion of functional end groups in the resulting polymers. In the case of P3AT, the living nature of the polymerization can be exploited to terminate the polymer chain with two different end groups. Future researches will focus on the synthesis of block copolymers by a postpolymerization coupling of the functional groups attached to the respective homopolymers.

Acknowledgment. We are grateful to the Katholieke Universiteit Leuven (GOA and CREA) and the Fund for Scientific Research (FWO-Vlaanderen) for financial support. A.F. and K.V.d.B. are doctoral fellows of IWT-Vlaanderen, and G.K. is postdoctoral fellow of the Fund for Scientific Research (FWO-Vlaanderen). P.G. and J.D.W. (FRS-FNRS research associate and research fellow) are grateful to the FRS-FNRS for financial support in the acquisition of the Waters QToF Premier mass spectrometer and for continuing support.

Supporting Information Available: NMR spectra of all new compounds and MALDI-ToF spectra of the polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Skotheim, T. A.; Reynolds, J. R. In *Handbook of Conducting Polymers*; CRC Press: Boca Raton, FL, 2007.

(2) Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, *38*, 8649–8656.

(3) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526–3528.

(4) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542–17547.

(5) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169–1171.

(6) Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Spiering, A. J. H.; van Dongen, J. L. J.; Vonk, E. C.; Claessens, H. A. *Chem. Commun.* **2000**, 81–82.

(7) Jeffries-EL, M.; Sauvé, G.; McCullough, R. D. *Adv. Mater.* **2004**, *16*, 1017–1019.

(8) Jeffries-EL, M.; Sauvé, G.; McCullough, R. D. *Macromolecules* **2005**, *38*, 10346–10352.

(9) Liu, J.; Sheina, E. E.; Kowalewski, T.; McCullough, R. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 329–332.

(10) Yokoyama, A.; Rato, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2008**, *41*, 7271–7273.

(11) Yokozawa, T.; Adachi, I.; Miyakoshi, R.; Yokoyama, A. *High Perform. Polym.* **2007**, *19*, 684–699.

(12) Wu, P.; Ren, G.; Li, C.; Mezzenga, R.; Jenekhe, S. A. *Macromolecules* **2009**, *42*, 2317–2320.

(13) Ouhib, F.; Khoukh, A.; Ledeuil, J.; Martinez, J.; Desbières, J.; Dagron-Lartigau, C. *Macromolecules* **2008**, *41*, 9736–9743.

(14) Ohshimizu, K.; Ueda, M. *Macromolecules* **2008**, *41*, 5289–5294.

(15) Zhang, Y.; Tajima, K.; Hirota, K.; Hashimoto, K. *J. Am. Chem. Soc.* **2008**, *130*, 7812–7813.

(16) Van den Bergh, K.; Huybrechts, J.; Verbiest, T.; Koeckelberghs, G. *Chem.—Eur. J.* **2008**, *14*, 9122–9125.

(17) Huang, L.; Wu, S.; Qu, Y.; Geng, Y.; Wang, F. *Macromolecules* **2008**, *41*, 8944–8947.

(18) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 753–765.

(19) Beryozkina, T.; Boyko, K.; Khanduyeva, N.; Senkovskyy, V.; Horecha, M.; Oertel, U.; Simon, F.; Stamm, M.; Kiriy, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 2695–2698.

(20) Beryozkina, T.; Senkovskyy, V.; Kaul, E.; Kiriy, A. *Macromolecules* **2008**, *41*, 7817–7823.

(21) Liu, J.; Loewe, R. S.; McCullough, R. D. *Macromolecules* **1999**, *32*, 5777–5785.

(22) Bronstein, H. A.; Luscombe, C. K. *J. Am. Chem. Soc.* DOI: 10.1021/ja9054977.

(23) Yokoyama, A.; Suzuki, H.; Kubota, Y.; Ohuchi, K.; Higashimura, H.; Yokozawa, T. *J. Am. Chem. Soc.* **2007**, *129*, 7236–7237.

(24) Doubina, N.; Ho, A., Jen, A. K.-Y.; Luscombe, C. K. *Macromolecules* DOI: 10.1021/ma901410k.

(25) Senkovskyy, V.; Khanduyeva, N.; Komber, H.; Oertel, U.; Stamm, M.; Kuckling, D.; Kiriy, A. *J. Am. Chem. Soc.* **2007**, *129*, 6626–6632.

(26) Van Soolingen, J. *Nickel-Catalysed Cyanation of Aryl Halides*; Utrecht, 1999.

(27) Meyer, G.; Rollin, Y.; Périchon, J. *J. Organomet. Chem.* **1987**, *33*, 263–267.

(28) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1960**, 1718–1729.

(29) Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324–4333.

(30) Khanduyeva, N.; Senkovskyy, V.; Beryozkina, T.; Horecha, M.; Stamm, M.; Uhrich, C.; Riede, M.; Leo, K.; Kiriy, A. *J. Am. Chem. Soc.* **2009**, *131*, 153–161.

(31) Khanduyeva, N.; Senkovskyy, V.; Beryozkina, T.; Bocharova, V.; Simon, F.; Nitschke, M.; Stamm, M.; Grötzschel, R.; Kiriy, A. *Macromolecules* **2008**, *41*, 7383–7389.

(32) Koeckelberghs, G.; Vangheluwe, M.; Samyn, C.; Persoons, A.; Verbiest, T. *Macromolecules* **2005**, *38*, 5554–5559.

(33) Vandeleene, S.; Van den Bergh, K.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2008**, *41*, 5123–5131.

(34) Miyakoshi, R.; Yokoyama, A.; Shimono, K.; Yokozawa, T. *J. Am. Chem. Soc.* **2006**, *128*, 16012–16013.

(35) Koeckelberghs, G.; Vangheluwe, M.; Van Doorsselaere, K.; Robijns, E.; Persoons, A.; Verbiest, T. *Macromol. Rapid Commun.* **2006**, *27*, 1920–1925.

(36) Since ^{1}H NMR spectroscopy indicates that no deprotection of the functional groups occurs during the polymerization, the deprotection, as observed in the MALDI-ToF spectra, must originate from the ionization during the MALDI-ToF experiment and not from the polymerization itself.

(37) Crabtree, R. H. In *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; John Wiley & Sons: New York, 2001; p 534.

(38) Tamao, K.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1958–1969.

(39) Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *Organometallics* **1983**, *2*, 1391–1396.