Incorporation of Different End Groups in Conjugated Polymers Using Functional Nickel Initiators — Source link ↗

Alfons Smeets, Karlien Van den Bergh, Julien De Winter, Pascal Gerbaux ...+2 more authors

Institutions: Katholieke Universiteit Leuven, University of Mons

Related papers:

- Chain-Growth Polymerization for Poly(3-hexylthiophene) with a Defined Molecular Weight and a Low Polydispersity

- Catalyst-transfer polycondensation. mechanism of Ni-catalyzed chain-growth polymerization leading to well-defined poly(3-hexylthiophene).

- Experimental evidence for the quasi-living nature of the grignard metathesis method for the synthesis of regioregular poly(3-alkylthiophenes)

- Chain Growth Mechanism for Regioregular Nickel-Initiated Cross-Coupling Polymerizations

- Externally initiated regioregular P3HT with controlled molecular weight and narrow polydispersity.

Share this paper: 📘 🐦 in ✉

Incorporation of different end-groups in conjugated polymers using functional nickel initiators

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

[a] Laboratory of Molecular Electronics and Photonics, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium

[b] Mass Spectrometry Center, Organic Chemistry Laboratory, University of Mons, 20 Place du Parc, B-7000 Mons, Belgium

guy.koeckelberghs@chem.kuleuven.be

Abstract. This manuscript investigates the use of arylnickel complexes for the synthesis of functionalized conjugated polymers is. The scope of the catalyst-transfer polycondensation of poly(3-alkylthiophene) using nickel was expanded by functionalizing and isolating the nickel initiator. *o*-Methyl substituted arylnickel complexes were isolated and used to initiate the polymerization of various substituted poly(thiophene)s and poly(*p*-phenylene). Finally, the living nature of the polymerization of poly(3-alkylthiophene) was exploited to prepare a polymer with two different end-groups – one arising from the Ni-initiator and one from the end-capper.

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]. Secondly, 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 all of the polymer chains are not 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.

2

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 transmetallation 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 2 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 is of crucial importance, since traces of any Ni^{+II} 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.
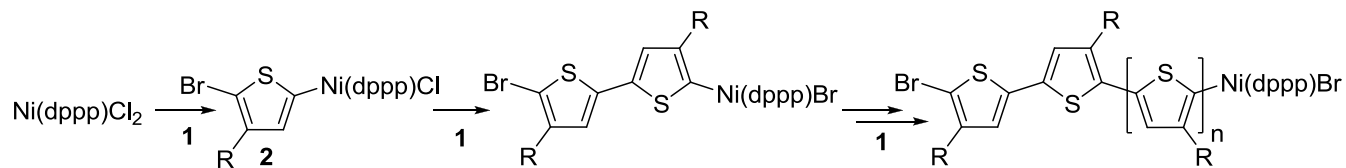
Scheme 1. Catalyst-transfer mechanism of poly(3-alkylthiophene)s. R = alkyl, dppp = 1,3-bis(diphenylphosphino)propane

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 (equation 1). In this process, Ni^{+II} salts are also formed, which can initiate the polymerization, resulting in polymer chains without a phenyl group.

$$2 \text{ PhNi(PPh}_3)_2\text{Br} \rightarrow \text{Ni} + 2\text{PPh}_3 + \text{Ph-Ph} + \text{Ni(PPh}_3)_2\text{Br}_2 \qquad \text{eq. 1}$$

This disproportionation can, however, be suppressed if an *o*-tolyl instead of a phenyl group is employed. In that case, 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 hour – the typical duration of a polymerization and far less 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$_3$]$_4$.
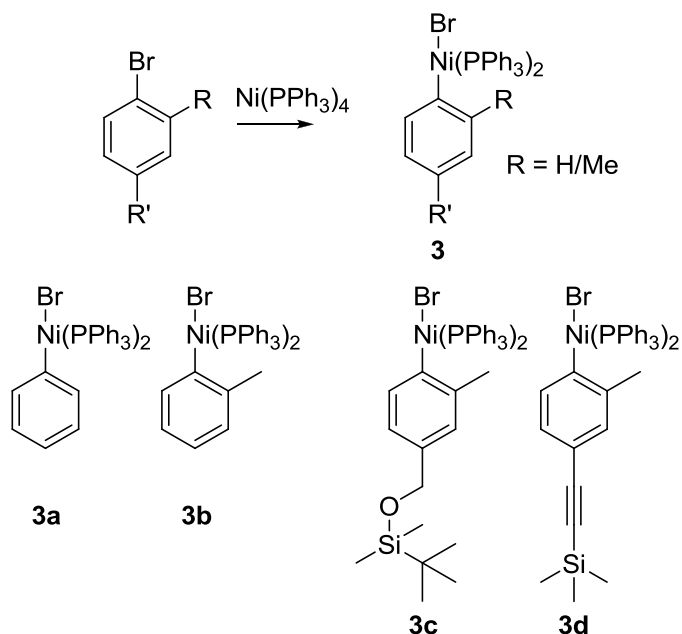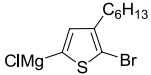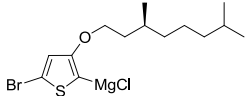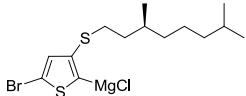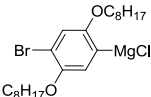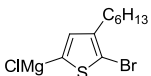

Scheme 2. Synthesis and structure of the Ni-initiators.

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 dialkoxy-benzenes[34], Table 1, entries 1-4). In all cases, polymers were recovered and the ^{1}H-NMR spectra (Supporting information) revealed the incorporation 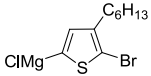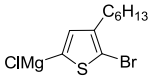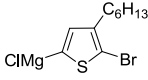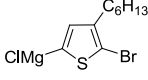of the initiator moiety. As can be derived from the MALDI-ToF (matrix-assisted laser light desorption ionization – time-of-flight) spectra (Supporting information) and summarized in Table 1, the polymer chains were mostly equipped with an *o*-tolyl end-group, demonstrating that **3b** was the dominant initiator and that little or no other initiators, which would result in Br/Br, Br/H and H/H end-cappings - such as Ni^{+II} 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 occurs.

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)	95%	0%	5%	0%

				1.8				
				1.7				
P7	C6H13 thiophene, ClMg—S—Br	**3c**	2 eq dppp	3.7 (1.3) 2.2 1.9	95%	0%	5%	0%
P8	C6H13 thiophene, ClMg—S—Br	**3d**	2 eq dppp	3.2 (1.3) 2.1 1.9	80%	10%	10%	0%
P9	C6H13 thiophene, ClMg—S—Br	**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, 78% for P4.

[b] of the samples after washing with acetone

[c] in THF toward poly(styrene) standards. The polydispersities are given between brackets. 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 reactions occurs.

[i] dppp = 1,3-bis(diphenylphosphino)propane

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 equivalents of dppp (Table 1, entries 5-6). 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 equivalents of dppp were added to suppress termination reactions. The ^{1}H NMR spectra revealed the incorporation of the functional groups, without any degradation nor 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 behaviour 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 tri-block copolymers composed of three different (conjugated)

blocks. Therefore, **1** was initiated by **3b** in the presence of 2 equivalents of dppp and the polymerization was quenched by the addition of 4-chloromagnesio-anisol, 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 polymer chains - the latter two arising from reaction of 4-chloromagnesio-anisol 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 post-polymerization coupling of the functional groups attached to the respective homopolymers.

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.

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

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*