Angewandte Chemie

DOI: 10.1002/anie.200804445

Reactive Polyolefins

Polyethylene Building Blocks by Catalyzed Chain Growth and Efficient End Functionalization Strategies, Including Click Chemistry

Rémi Briquel, Jérôme Mazzolini, Tristana Le Bris, Olivier Boyron, Fernande Boisson, Frédéric Delolme, Franck D'Agosto, Christophe Boisson, and Roger Spitz*

Polyethylene and polypropylene are the largest volume thermoplastics manufactured in the world, and new polymer materials based on these polymers could have a strong impact on our everyday life. The combination of the excellent chemical and physical properties of polyolefins along with their low cost of manufacture makes this class of polymer very attractive for commercial purposes. The modification of polyolefins has always been both an academic and an industrial challenge.[1a] The scientific difficulty is due to the fact that functional or polar groups can hardly be incorporated into these materials when produced industrially by catalytic olefin polymerization.[1b] The development of new strategies to incorporate polar segments into polyolefins in a controlled fashion is one of the long-term goals in polymer chemistry, since the materials would exhibit new architectures with many desirable properties.[1a] Some of the existing methods to produce polyolefins bearing polar groups or segments are based on the use of reactive polyolefins.[1c] The functional polyolefins can serve as building blocks for constructing multisegmented polymers or more complex architectures based on polyolefins. The difficulty lies in finding an efficient and simple way of introducing appropriate functional groups, such as reactive or polymerizable groups, and initiators or control agents for other polymerization techniques.

The possibility of taking advantage of the reactivity of carbon–metal bonds in catalytic olefin polymerization processes has been enhanced by the discovery of specific features, such as chain-shuttling events in the forming chains between the active metal and a second metal center, in certain catalytic systems.[2] To make the most of this particular concept of chain shuttling, dipolyethylenylmagnesium compounds (PE-Mg-PE) were prepared by the polymerization of ethylene using the $[(C_5Me_5)_2NdCl_2Li(OEt_2)_2]$ complex in combination with *n*-butyloctylmagnesium (BOMg).

Although not originally exploited,[3] the nucleophilicity of the carbon moiety in PE-Mg-PE has been reported to favor the introduction of various functional groups at the end of the PE chain.[4] Narrowly distributed (PDI < 1.2) short alkyl chains to crystalline polyethylene (up to 5000 $\mathrm{g\,mol^{-1}}$) can be synthesized with this catalytic system, and we report here the implementation of very simple strategies for the end-functionalization of these chains (Scheme 1), which will enable their further modification or incorporation into more complex architectures. Examples of 1) functionalized polyethylene, 2) polymerizable polyethylene, and 3) control agents for free-radical polymerization based on polyethylene are given below.

We discovered that the addition of iodine after polyethylene catalyzed chain growth on magnesium led to highly functionalized end-halogenated polyethylene (PE-I). This successful introduction of an iodide atom was confirmed by the ^{1}H NMR spectrum (Figure 1), which showed a triplet at $\delta = 3.00$ ppm corresponding to the methylene group adjacent to the iodine atom. Degrees of functionalization ranging from 73.0% up to 96.8%, as determined by ^{1}H NMR spectroscopic analysis, demonstrated the efficiency of the end-functionalization. The decrease in the degree of functionalizationwith an increasing molar mass of the polyethylene correlates with the use of lower Mg/Nd ratios. The control of the polymerization being less efficient, an increase in the proportion of product with a vinyl group at the chain end as a result of β-H elimination during the catalytic process is observed. The obtained PE-I chains, in which the chain end is now electrophilic, open the way to a much broader range of possible reactions, including those involving nucleophilic attack.

These reactions include the simple introduction of an azide end group by reaction with NaN_3. As shown by ^{1}H NMR analysis (Figure 1), an almost quantitative substitution of the iodine atom by an azide group (Table 1) resulted from heating a mixture of PE-I and NaN_3 in DMF at reflux for two hours. This successful substitution was also confirmed by FTIR analysis of PE-N_3 (see the Supporting Information), which showed, along with the expected PE absorption bands, an additional band corresponding to -N_3 at 2095 $\mathrm{cm^{-1}}$.

These newly synthesized PE-N_3 compounds can very easily and quantitatively be reduced with $LiAlH_4$ to give functional chains with an amine end group (PE-NH_2). The disappearance of the azide band in the FTIR spectra was evident. Furthermore, in the ^{1}H NMR spectra, the resonance corresponding to the methylene group adjacent to the azide

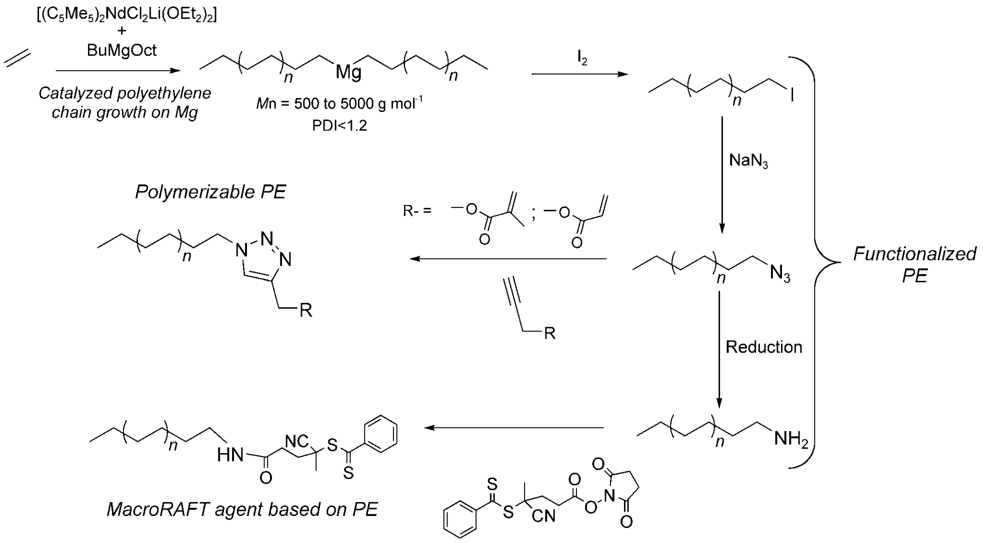
---

[*] R. Briquel, J. Mazzolini, T. Le Bris, O. Boyron, Dr. F. D'Agosto, Dr. C. Boisson, Dr. R. Spitz
Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR
5265 Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2), LCPP team
Bat 308F, 43 Bd du 11 novembre 1918, 69616 Villeurbanne (France)
Fax: (+33) 4-72-43-17-70
E-mail: dagosto@lcpp.cpe.fr
Homepage: http://www.lcpp-cpe.com

Dr. F. Boisson
Service de RMN du Réseau des Polyméristes Lyonnais
CNRS UMR5223 (France)

F. Delolme
CNRS USR 59 SCA, Echangeur de Solaize, Chemin du canal
69360 Solaize (France)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200804445.



Scheme 1. General strategy.

end group disappeared while a resonance appeared at $\delta = 2.78$ ppm corresponding to the methylene group adjacent to the introduced amine end group. These observations thus demonstrate the successful formation of PE-NH_2 (see Table 1 and the corresponding analyses in the Supporting Information).

The resulting functionalized polyethylenes (PE-I, PE-N_3, PE-NH_2) are interesting starting points to expand the range of reactive polyolefins. As an example, PE-N_3 has been evaluated in highly efficient click reactions[5] involving a Huisgen [1,3] cycloaddition with alkyne-containing reagents. Thus, commercially available propargyl acrylate and propargyl methacrylate were treated with PE-N_3 in the presence of $CuSO_4$ and sodium ascorbate in DMF at 130 °C. The resulting products (PE-A and PE-M) were all characterized by FTIR and ^1H NMR spectroscopy as well as by MALDI-TOF mass spectrometry (see the Supporting Information).

Acrylate functionalization at the chain end was supported by the disappearance of the azide band at 2095 cm^{-1} and the presence of a carbonyl band at 1732 cm^{-1} and of a $CH_2{=}CH$ band at 1634 cm^{-1} in the IR spectrum of the resulting polyethylene. A comparison of the ^1H NMR spectra of starting PE-N_3 and the obtained product shows the complete disappearance of the signal corresponding to the methylene group (at $\delta = 3.05$ ppm) adjacent to the azide group. The observation in the ^1H NMR spectrum of a signal at $\delta = 7.22$ ppm for the triazole proton and two signals at $\delta = 4.00$ ppm and 5.22 ppm that could be assigned to methylene groups adjacent to the triazole ring, together with the corresponding integrals, support the complete assignments proposed in Figure 1 and the Supporting Information, and show that the acrylate moiety had successfully been introduced in a yield of 95.3 %. MALDI-TOF mass spectrometry analysis was successfully performed on PE-A and PE-M; this technique is seldom used for this kind of polymer, which lacks functional groups that can complex cations. Very clean spectra were obtained and the main, and almost exclusive, population observed corresponds to the expected one (see the Supporting Information), and is thus consistent with the structure proposed on the basis of the NMR data, and illustrates the success of the reaction. The tolerance, versatility, and cleanliness of the reaction together with it being quantitative fulfil the requirements for click chemistry.[5] In addition, the extraordinary short reaction times required (less than 15 min) to perform the Huisgen [1,3] cycloaddition makes this polyethylene functionalization pathway a very attractive one. This is the first report on polyethylene functionalization using click chemistry. The proof of concept that such compounds can genuinely be used as building blocks was provided by showing that these macromonomers can be readily (co)polymerized, for example, by free-radical polymerization. Thus, PE-M was copolymerized with methyl methacrylate (MMA) in toluene by using azobis(isobutyronitrile) (AIBN) as an initiator (see the Supporting Information). After three hours of reaction at 85 °C, the MMA was completely consumed. Analysis of the polymerization medium by size-exclusion chromatography (SEC) revealed the presence of two populations: PE-M starting material ($M_n = 1040$, PDI = 1.19, PE calibration) and an additional population with $M_n = 20\,000$ $g\,mol^{-1}$ (PDI = 2.0, universal calibration). To determine if PE-M is effectively inserted into the newly formed polymer, the conversion of PE-M was determined by analyzing the residue of the polymerization medium by ^1H NMR spectroscopy after drying. According to the obtained spectrum, a copolymer was formed effectively and 76 % of the starting PE-M was inserted into the PMMA backbone; this value corresponds to 2.4 % PE units.

A dithioester end group, which can control the free-radical polymerization of a broad range of monomers in the reversible addition-fragmentation chain transfer (RAFT) process, was introduced by reaction of PE-NH_2 with an activated ester containing a RAFT agent (Scheme 1) through a mechanism reported previously by our research group.[6] The success of the reaction, as confirmed by ^1H NMR analyses of the resulting product (see the Supporting Information), makes the elaboration of a broad range of block copolymers possible, which we are currently studying. As an example, *n*-butyl acrylate was polymerized using PE substituted with a RAFT group (PE-NH-RAFT) to mediate a RAFT process. This experiment was compared to a blank experiment performed under the same conditions with unfunctionalized polyethylene instead of PE-NH-RAFT. While the medium rapidly turned into a gel in the control experiment (uncontrolled polymerization), the PE-NH-RAFT-mediated polymerization medium remained slightly

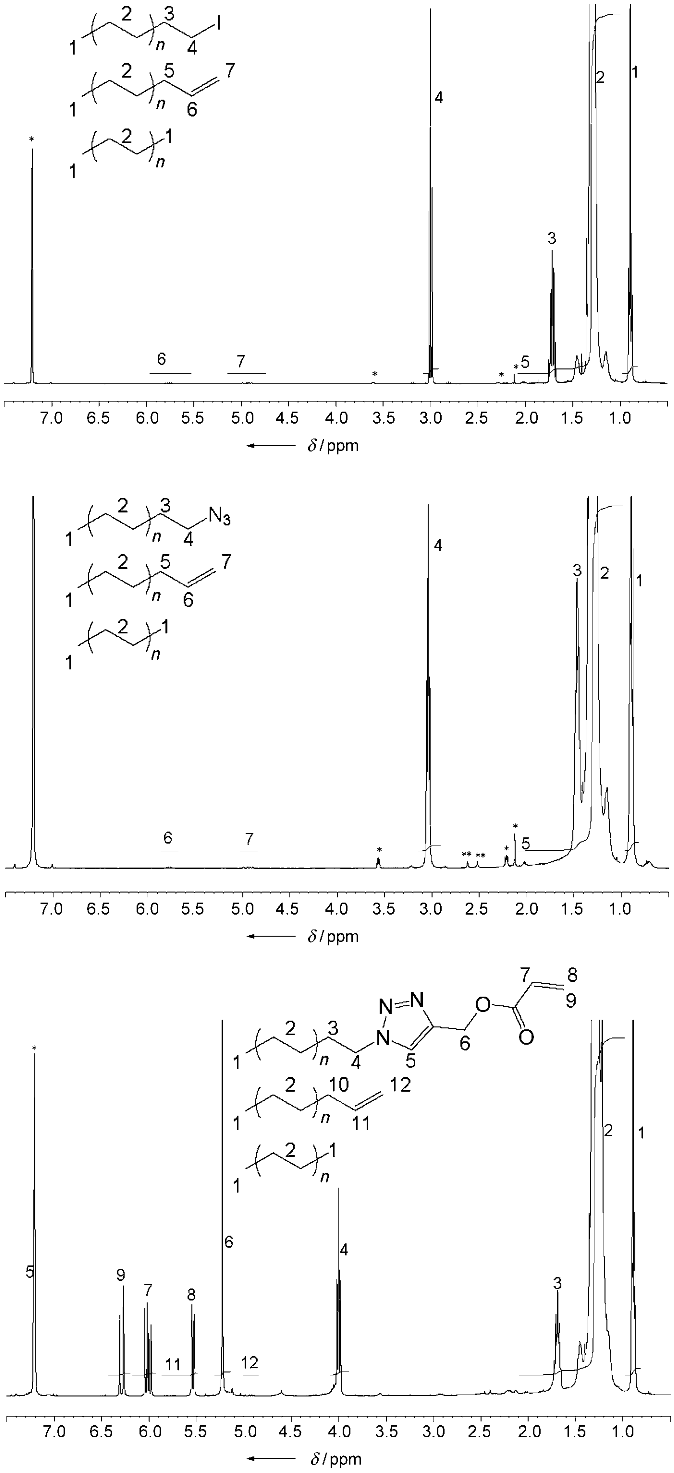


Figure 1. ^{1}H NMR (C_6D_6/TCE 1:2 v/v, 400 MHz, number of scans = 1024, 363 K) spectra of a) PE-I, b) PE-N_3, and c) PE-acrylate. Starting PE-I = sample 1 in Table 1. Signals marked by an asterisk are solvent impurities.

Table 1: Molar mass characteristics and yields of end-functionalized polyethylene and end-functionalization for PE-I, PE-N_3, and PE-NH_2

Entry	M_n[a] [g mol^{-1}] (X_n)[a]	M_n[b] [g mol^{-1}] (PDI)[b]	% PE-I[c]	% PE-N_3[c] (yield %)[d]	% PE-NH_2[c] (yield %)[d]
1	1148 (41)	1020 (1.23)	96.8	94.1 (97.2)	94.1 (100)
2	2296 (82)	2230 (1.26)	86.7	86.0 (99.2)	85.8 (99.8)
3	4536 (162)	4980 (1.37)	73.0	68.4 (93.6)	n.d.

[a] M_n values of the alkyl chain of functionalized PE determined by ^{1}H NMR spectroscopy and the corresponding degree of polymerization (X_n). [b] M_n value of PE-I determined by high-temperature SEC analyses and the corresponding polydispersity index (PDI). [c] Functional group. [d] Reaction yields. n.d.: not determined.

viscous up to the end of the polymerization (see the Supporting Information). As shown by the observed increase in the molar masses versus conversion together with the obtained low PDI (see the Supporting Information), the growth of the chains is controlled by the PE-NH-RAFT moiety.

In conclusion, the use of a polyethylene catalyzed chain growth on magnesium in combination with simple and efficient functionalization strategies enables the synthesis in high yield of polyethylenes highly end-functionalized with iodine, azide, or amine groups. The functional groups can then be reacted further by using modular chemistry approaches to generate new functional polyolefins that can be used as building blocks for the design of macromolecular architectures.

Received: September 9, 2008

Keywords: catalysis · click chemistry · macromonomers · polymers · RAFT polymerization

---

[1] a) T. C. Chung, *Prog. Polym. Sci.* **2002**, *27*, 39–85; b) A. Berkefeld, S. Mecking, *Angew. Chem.* **2008**, *120*, 2572–2576; *Angew. Chem. Int. Ed.* **2008**, *47*, 2538–2542; c) R. Godoy Lopez, F. D'Agosto, C. Boisson, *Prog. Polym. Sci.* **2007**, *32*, 419–454.

[2] a) G. J. P. Britovsek, S. A. Cohen, V. C. Gibson, P. J. Maddox, M. Van Meurs, *Angew. Chem.* **2002**, *114*, 507–509; *Angew. Chem. Int. Ed.* **2002**, *41*, 489–491; b) V. C. Gibson, *Science* **2006**, *312*, 703–704; c) D. J. Arriola, E. M. Carnahan, P. D. Hustad, R. L. Kuhlman, T. T. Wenzel, *Science* **2006**, *312*, 714–719.

[3] J. F. Pelletier, A. Mortreux, X. Olonde, K. Bujadoux, *Angew. Chem.* **1996**, *108*, 1980–1982; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1854–1856.

[4] a) R. Godoy Lopez, C. Boisson, F. D'Agosto, R. Spitz, F. Boisson, D. Gigmes, D. Bertin, *J. Polym. Sci. Part A* **2007**, *45*, 2705–2718; b) R. Godoy Lopez, C. Boisson, F. D'Agosto, R. Spitz, F. Boisson, D. Gigmes, D. Bertin, *Macromol. Rapid. Commun.* **2006**, *27*, 173–181.

[5] a) H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem.* **2001**, *113*, 2056–2075; *Angew. Chem. Int. Ed.* **2001**, *40*, 2004–2021; b) M. Meldal, *Macromol. Rapid Commun.* **2008**, *29*, 1016–1061; c) W. H. Binder, R. Sachsenhofer, *Macromol. Rapid Commun.* **2008**, *29*, 952–981.

[6] M. Bathfield, F. D'Agosto, R. Spitz, M. T. Charreyre, T. Delair, *J. Am. Chem. Soc.* **2006**, *128*, 2546–2547.