Derivatization of Polymers

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Divinyl-End-Functionalized Polyethylenes: Ready Access to a Range of Telechelic Polyethylenes through Thiol–Ene Reactions**

Sebastien Norsic, Coralie Thomas, Franck D'Agosto, and Christophe Boisson**

Abstract: *Telechelic α,ω-iodo-vinyl-polyethylenes (Vin-PE-I) were obtained by catalytic ethylene polymerization in the presence of [$(C_5Me_5)_2NdCl_2Li(OEt_2)_2$] in combination with a functionalized chain-transfer agent, namely, di(10-undecenyl)magnesium, followed by treatment of the resulting di(vinylpolyethylenyl)magnesium compounds ((vinyl-PE)$_2$-Mg) with I_2. The iodo-functionalized vinylpolyethylenes (Vin-PE-I) were transformed into unique divinyl-functionalized polyethylenes (Vin-PE-Vin) by simple treatment with tBuOK in toluene at 95 °C. Thiol–ene reactions were then successfully performed on Vin-PE-Vin with functionalized thiols in the presence of AIBN. A range of homobifunctional telechelic polyethylenes were obtained on which a hydroxy, diol, carboxylic acid, amine, ammonium chloride, trimethoxysilyl, chloro, or fluoroalkyl group was installed quantitatively at each chain end.*

With more than 120 million tons produced each year, polyolefins remain by far the most important class of thermoplastics.[1] Despite this great popularity, the ready introduction of reactive groups into these nonpolar materials is still an important target. Indeed, the addition of functionality to polyolefins is a way to widen the field in which polyolefinic materials may be applied, either by direct use of the obtained polymers or by their use as a nonvolatile additive in polyolefin batches.

Several methods have been investigated for the production of functionalized polyolefins.[2] Among them, the most valuable are of course those which take into account as much as possible the industrial constraints (cost of production and of raw materials). A limited range of functionalized polyolefins are produced by either radical polymerization of ethylene and polar monomers, such as vinyl acetate, under harsh conditions or postmodification by reactive extrusion;[3] however, as far as we know, there are no industrially viable equivalent products produced by olefin-polymerization catalysis.[4]

The field of olefin-polymerization catalysis has witnessed the development of controlled olefin polymerization under catalytic conditions, namely, coordinative chain-transfer polymerization (CCTP)[5] or catalyzed chain growth (CCG),[6] as originally coined by Samsel et al.[7] Control of the polymerization is based on a mechanism of degenerative transfer, which is similar to the process of reversible addition–fragmentation chain transfer (RAFT) in controlled radical polymerization.[8] An organometallic species is used as a chain-transfer agent in a system that is insensitive to the well-known and intrinsic β-H elimination reaction. After the consumption of the required quantity of the olefin for the production of polymers with the targeted molar mass, the polyolefin chains are thus bound to a metal center.[5a,6a,9] We have taken advantage of the reactivity of polymer chains bound to a metal to develop a range of chemical tools for the end-functionalization of polyethylene chains.[10] The catalytic system of [$(C_5Me_5)_2NdCl_2Li(OEt_2)_2$] in combination with (*n*-butyl)(*n*-octyl)magnesium[9] was used to produce di(polyethylenyl)magnesium (PE_2Mg) according to a catalyzed chain-growth process in which the chains grow on the Nd center and are reversibly transferred to magnesium. We also recently demonstrated that the selective and quantitative introduction of a vinyl group at the α position of polyethylene chains is possible by CCG of polyethylene onto a neodymium-based catalyst in the presence of a functionalized chain-transfer agent (CTA), namely, di(10-undecenyl)magnesium. A functionality was further installed at the ω chain end simply by deactivation of the formed di(vinylpolyethylenyl)magnesium compounds ((vinyl-PE)$_2$Mg). This synthesis was the first example of the production of telechelic polyethylenes by polymerization catalysis of ethylene.[11] Heterobifunctional telechelic polyethylenes with a vinyl α end group and a −I, $-N_3$, $-NH_2$, −SC(=S)NEt$_2$, or −SC(=S)OEt group at the ω chain end were obtained in high yield. A different strategy based on the use of zinc complexes as chain-transfer agents to prepare telechelic polyethylenes was described shortly after this first report.[12]

The vinyl functionality possesses the double advantage that it remains a reactive group even though the corresponding polymers can be stored easily. When an olefin is polymerized by coordination catalysis, side reactions of β-H transfer (elimination or transfer to the monomer) intrinsically lead to the formation of vinyl-terminated polyolefins. Several attempts have thus been made to render this reaction quantitative and take advantage of the formation of these chains for the further introduction of functional groups[13,14] and have showed the usefulness of such a group for further

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[*] Dr. S. Norsic, Dr. C. Thomas, Dr. F. D'Agosto, Dr. C. Boisson
Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, UMR 5265
C2P2 (Chemistry, Catalysis, Polymers, and Processes), Team LCPP
Bat 308F, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne (France)
E-mail: franck.dagosto@univ-lyon1.fr
christophe.boisson@univ-lyon1.fr

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functionalization.[15] Recently, Bazan and co-workers[16] showed that α,ω-divinyl-functionalized polyolefins could be obtained by a strategy based on the depolymerization of unsaturated polyolefins,[17] such as copolymers of ethylene, 1-octene, and butadiene, in the presence of olefin, metathesis catalysts in combination with ethylene (ethenolysis).

Herein, we report the facile preparation of these unique divinylpolyethylene building blocks with a vinyl group at each chain end. This material was then used as a reactant for the design of a vast range of homotelechelic polyethylenes on the basis of thiol–ene chemistry.[14a]

Neodymium metallocenes have shown a unique ability to catalyze polyethylene-chain growth on dialkyl magnesium compounds used as chain-transfer agents.[9] We recently reported the use of di(10-undecenyl)magnesium ($CH_2{=}CH(CH_2)_9)_2Mg$, BUM) as an original dialkenyl magnesium chain-transfer agent (CTA) for the quantitative synthesis of well-defined vinyl-terminated polyethylenes.[11] The integrity of the vinyl group was maintained by tuning the number of methylene groups between the metal and the vinyl group in the dialkenyl magnesium reagent to preclude the formation of thermodynamically favored five- or six-membered rings.[11]

The polymerization of ethylene with $[(C_5Me_5)_2NdCl_2Li(OEt_2)_2]$ and BUM (Mg/Nd 150:1) in toluene was commenced at 75 °C and proceeded rapidly to produce di(vinylpolyethylenyl)magnesium ((Vin-PE)$_2$Mg). Iodo end-functionalization is valuable, since it turns the nucleophilic end carbon atom of PE$_2$Mg into an electrophilic carbon atom in PE-I.[10f] Furthermore, the reaction was performed directly in the reactor after ethylene polymerization, with simple I_2 as the reactant, and led to highly functionalized PE chains ($>90\,\%$).

The (Vin-PE)$_2$Mg intermediate was thus subjected to cooling to 10 °C, followed by stirring with an iodine solution in THF for 1 h. As expected, high functionality of Vin-PE-I was observed ($>93\,\%$) for a range of targeted molar masses (experiments A, B, and C in Table 1). Low dispersities were observed in each case ($Đ<1.18$). The introduction of chain ends on a short PE molecule may impact the elution of the resulting polymers and explain slight discrepancies observed between the M_n values determined by ^1H NMR spectroscopy and size-exclusion chromatography (SEC), whereby the latter data were obtained on the basis of PE calibration.

Table 1: Characteristics of vinyl-terminated telechelic polyethylenes.

Vin-PE-X	M_n [g mol^{-1}]	M_n [g mol^{-1}][b]	$Đ$[b]	Vinyl—[c]	—I[c]	$-CH_3$[c]
A (X=I)	930[a]	640	1.15	1	0.95	0.05
B (X=I)	1340[a]	980	1.15	1	0.95	0.05
C (X=I)	2430[a]	1860	1.18	1	0.93	0.07
A′ (X=Vin)	870[c]	625	1.15	1.95	–	0.05
B′ (X=Vin)	1600[c]	1220	1.16	1.95	–	0.05
C′ (X=Vin)	2490[c]	1900	1.22	1.91	–	0.09

[a] The number-average molar mass (M_n) was determined by ^1H NMR analysis of Vin-PE-I by integration of the signals for the main methylene hydrogen atoms ($I_{-(CH_2)-}$), for the vinyl hydrogen atoms ($I_{CH_2=CH-}$), and for the methylene group adjacent to the iodo group (I_{-CH_2-I}), and by using the equation $M_n=21\,[(I_{-(CH_2)-}+I_{-CH_2-I})/I_{CH_2=CH-}]+154$. [b] The M_n value was determined by high-temperature SEC (HTSEC) by using PE standards. [c] The M_n value was determined by ^1H NMR analysis of Vin-PE-Vin by integration of the signals for the main methylene hydrogen atoms ($I_{-(CH_2)-}$) and for the vinyl hydrogen atoms ($I_{CH_2=CH-}$), and by using the equation $M_n=42\,[I_{-(CH_2)-}/I_{CH_2=CH-}]+54$.

These iodo-functionalized vinylpolyethylenes (Vin-PE-I) were treated with potassium *tert*-butoxide (*t*BuOK, 10 equiv) in toluene at 90 °C. As attested by ^1H NMR spectroscopic analysis (Figure 1), the resonances of the methylene groups adjacent to and at the β position to the iodo group (at 2.94 and 1.66 ppm, respectively, in Figure 1 a) completely disappeared in the spectrum of the obtained divinylpolyethylenes (Vin-PE-Vin, in Figure 1 b).

^{13}C NMR spectroscopic analysis confirmed the quantitative transformation of the iodo chain end into a vinyl end group (see Figures S1 and S2 in the Supporting Information), as attested by the disappearance of the characteristic carbon resonance of the methylene group adjacent to the iodo group at 4.96 ppm (see Figure S1). The desired divinylpolyethylenes were thus readily obtained through quantitative transformation of the iodo group (A′, B′, and C′ in Table 1). The employed chemistry does not affect the integrity of the main chain, as similar molar masses to those of the starting Vin-PE-I polymers were observed for the product and remained narrowly distributed ($Đ<1.22$).

Up to now, the main methods for the synthesis of telechelic PEs have involved polymerization of butadiene, followed by functionalization and hydrogenation,[18] or partial hydrogenation of polybutadiene, followed by degradation of the internal double bond by metathesis,[18] or ring-opening metathesis polymerization of a cyclic olefin, followed by functionalization and hydrogenation.[19] In these strategies, systematic recourse to a hydrogenation step to generate the polyethylene chain would require the vinyl groups to be installed after hydrogenation. These new Vin-PE-Vin building blocks are unprecedented and have the advantage of being obtained after a single chemical step following the deactivation of the ethylene-polymerization reaction mixture with I_2.

As mentioned above, the reactivity of end vinyl groups carried by polyolefin chains has already been evaluated, in particular by the use of thiol–ene chemistry for polyethylene or polypropylene.[13f,14,20] With a view to designing original PE-based building blocks, we naturally evaluated the reactivity of the new divinylpolyethylenes by subjecting them to thiol–ene reactions with functional thiols.

In the field of polymer science, alcohols are employed as efficient initiating sites for the ring-opening polymerization of heterocycles or as a starting reactive group for further transformations. Therefore, hydroxy-end-functionalized polyolefins are of interest for the synthesis of block copolymers. This OH group can be introduced onto polyolefins by oxidation of the metal–carbon bond with dry air.[21] However, this reaction proceeds in moderate yield ($<80\,\%$ functionality) and through the potential formation of explosive peroxides. To introduce hydroxy groups at both chain ends of PE, we thus treated Vin-PE-Vin with mercaptoethanol (10 equiv) in the presence of azobisisobutyronitrile (AIBN, 0.5 equiv) as a radical source. The polymer recovered was

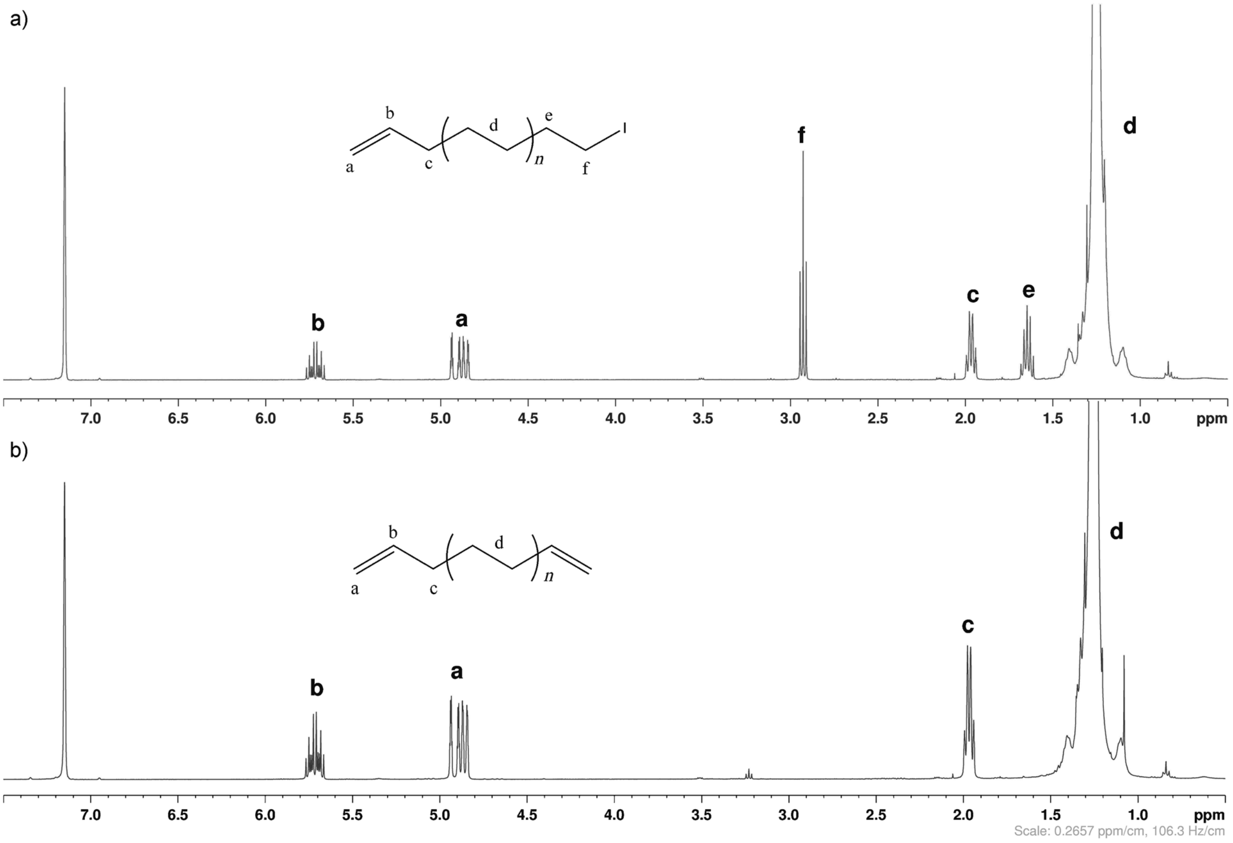


Figure 1. ^{1}H NMR spectrum of a) product C (Vin-PE-I) and b) product C′ (Vin-PE-Vin).

analyzed by ^{1}H NMR spectroscopy (Figure 2) and compared to the starting polymer Vin-PE-Vin (Figure 1 b).

The resonances of the starting vinylic hydrogen atoms completely disappeared in the spectrum of the final product, which showed the expected resonances of the polyethylene main chain (−CH_2−CH_2− at 1.24 ppm). The formation of the thioether was confirmed by the presence of triplets at 2.47 and 2.34 ppm due to the methylene groups next to the sulfur atoms (−CH_2−S−CH_2−) and the presence of the hydroxy functionality with the associated resonance of the methylene group adjacent to the OH group (-CH_2-OH at 3.48 ppm). Quantitative functionalization was also observed by ^{13}C NMR analysis (see Figure S3), thus showing the superiority of this strategy as compared to the aforementioned carbon–metal-oxidation routes. This successful transformation also

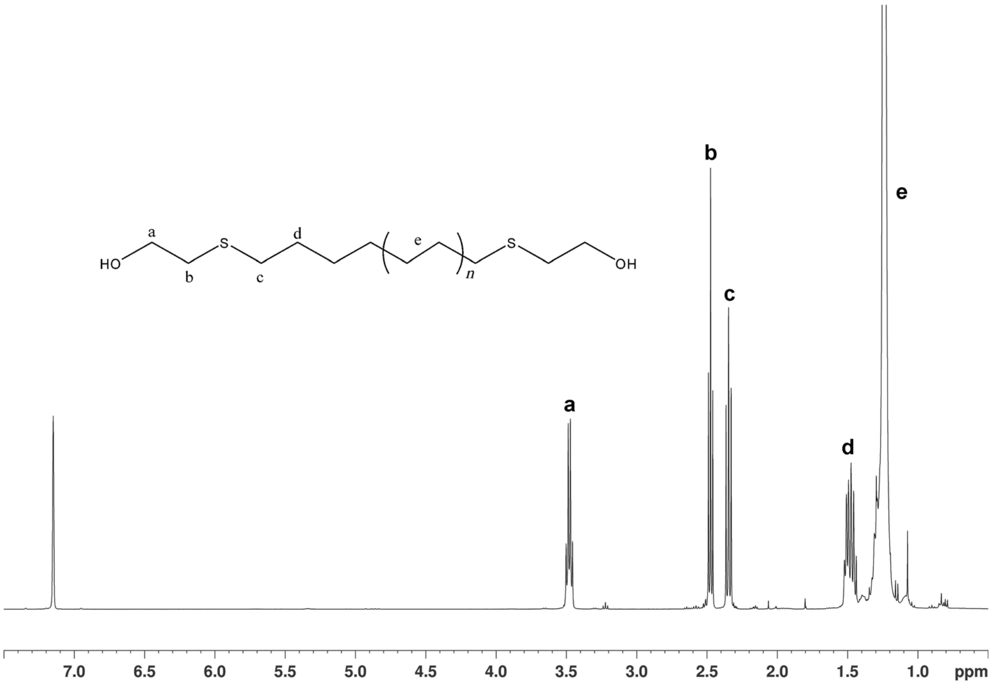
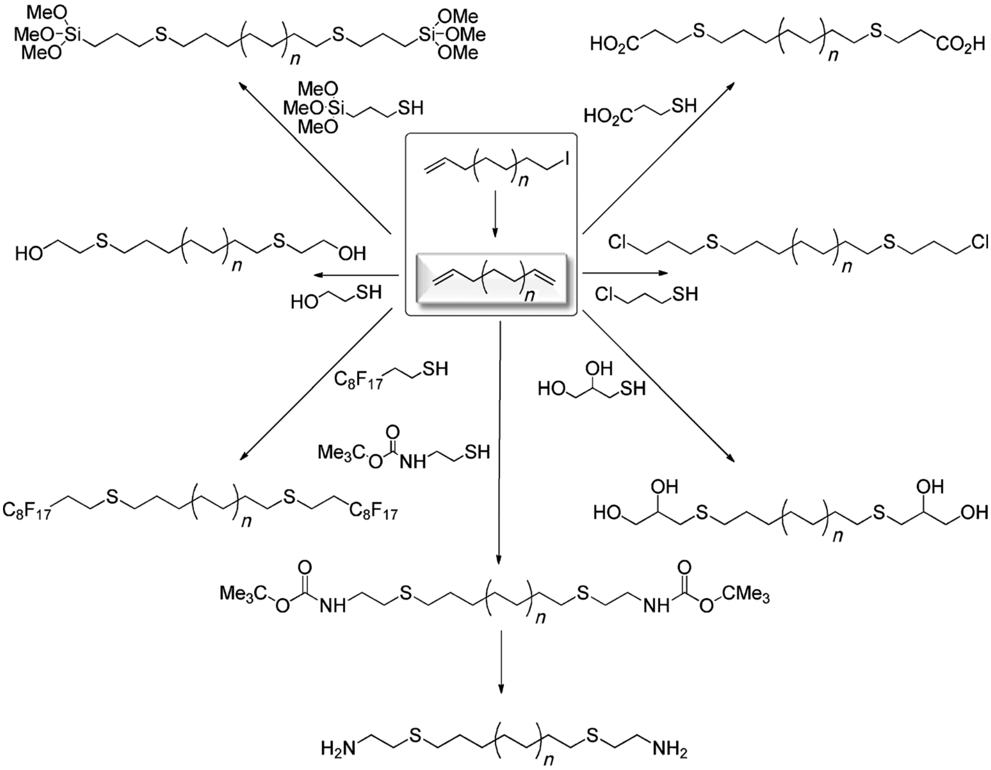


Figure 2. ^{1}H NMR spectrum of HO-PE-OH.



Scheme 1. Homobifunctional telechelic polyethylenes obtained by the thiol–ene reaction of various functional thiols with divinyl telechelic polyethylene.

shows the potential of these divinylpolyethylenes as intermediates for the synthesis of other telechelic PEs of interest. On the basis of these results, we investigated the reaction of a range of reactive thiols, such as 3-mercaptopropionic acid, 2-mercaptoethanol, 1-thioglycerol, 3-chloro-1-propanethiol, 2-(*tert*-butoxycarbonylamino)ethanethiol, 2-mercaptoethylamine hydrochloride, (3-mercaptopropyl)trimethoxysilane, and 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (Scheme 1). All functionalization reactions were performed under the same conditions, and all but two proceeded quantitatively (see Figures S4–S10).

The addition of thioglycolic acid to the vinyl groups in the presence of AIBN did not occur to 100% functionalization (maximum of 95%). The number of methylene spacers between carboxylic acid and the thiol groups was then advantageously increased by the use of 3-mercaptopropionic acid. The addition reaction then led quantitatively to the desired product HCOOC-PE-COOH under the same experimental conditions.

The addition of cysteamine and cysteamine hydrochloride to Vin-PE-Vin failed. The presence of HCl in the reagent makes it hygroscopic and also only weakly reactive in this thiol–ene radical addition, as observed previously.[22] The use of the neutral compound 2-(*tert*-butoxycarbonylamino)ethanethiol led to the quantitative functionalization of Vin-PE-Vin (see Figure S7). After deprotection with acidic methanol, followed by neutralization with sodium hydroxide, the targeted polmer NH_2-PE-NH_2 was obtained quantitatively (see Figure S8).

In summary, we have reported herein a facile strategy for the synthesis of α,ω-divinyl telechelic polyethylenes from polyethylene by catalyzed chain growth after simple and efficient treatment with iodine and *t*BuOK. The resulting vinyl end groups were readily transformed into a variety of reactive functionalities. The synthesized homobifunctional telechelic polyethylenes were characterized completely by ^{1}H and ^{13}C NMR spectroscopy and by HTSEC. This strategy provides a generic and viable route to designed reactive polyethylene chains that may offer numerous advantages in the vast field of the application of polyolefin-based materials, including the use of telechelic PEs as comonomers, chain-branching agents, cross-linking agents, and additives as surface modifiers and for the dispersion of fillers in polyolefins.

Keywords: functionalization · polyethylene · polymerization · telechelic polymers · thiol–ene reactions

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[1] Petroleum and Petrochemicals Economics Program: Petrochemical Market Dynamics; Polyolefins 2012; ChemSystems; July 2012.

[2] a) N. K. Boaen, M. A. Hillmyer, *Chem. Soc. Rev.* **2005**, *34*, 267–275; b) P. Atallah, K. B. Wagener, M. D. Schulz, *Macromolecules* **2013**, *46*, 4735–4741; c) T. C. M. Chung, *Macromolecules* **2013**, *46*, 6671–6698.

[3] E. Passaglia, S. Coiai, S. Augier, *Prog. Polym. Sci.* **2009**, *34*, 911–947.

[4] B. P. Carrow, K. Nozaki, *Macromolecules* **2014**, *47*, 2541–2555.

[5] a) L. R. Sita, *Angew. Chem. Int. Ed.* **2009**, *48*, 2464–2472; *Angew. Chem.* **2009**, *121*, 2500–2508; b) P. D. Hustad, *Science* **2009**, *325*, 704–707; c) F. Alfano, H. W. Boone, V. Busico, R. Cipullo, J. C. Stevens, *Macromolecules* **2007**, *40*, 7736–7738.

[6] a) R. Kempe, *Chem. Eur. J.* **2007**, *13*, 2764–2773; b) A. Valente, A. Mortreux, M. Visseaux, P. Zinck, *Chem. Rev.* **2013**, *113*, 3836–3857; c) D. J. Arriola, E. M. Carnahan, P. D. Hustad, R. L. Kuhlman, T. T. Wenzel, *Science* **2006**, *312*, 714–719.

[7] E. G. Samsel (Ethyl Corp., USA), EP539876, **1993**.

[8] F. D'Agosto, C. Boisson, *Aust. J. Chem.* **2010**, *63*, 1155–1158.

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

[10] a) J. Mazzolini, O. Boyron, V. Monteil, F. D'Agosto, C. Boisson, G. C. Sanders, J. P. A. Heuts, R. Duchateau, D. Gigmes, D. Bertin, *Polym. Chem.* **2012**, *3*, 2383 – 2392; b) D. Damiron, J. Mazzolini, F. Cousin, C. Boisson, F. D'Agosto, E. Drockenmuller, *Polym. Chem.* **2012**, *3*, 1838 – 1845; c) M. Bieligmeyer, S. M. Taheri, I. German, C. Boisson, C. Probst, W. Milius, V. Altstaedt, J. Breu, H.-W. Schmidt, F. D'Agosto, S. Förster, *J. Am. Chem. Soc.* **2012**, *134*, 18157 – 18160; d) M. M. Unterlass, E. Espinosa, F. Boisson, F. D'Agosto, C. Boisson, K. Ariga, I. Khalakhan, R. Charvet, J. P. Hill, *Chem. Commun.* **2011**, *47*, 7057 – 7059; e) J. Mazzolini, E. Espinosa, F. D'Agosto, C. Boisson, *Polym. Chem.* **2010**, *1*, 793 – 800; f) R. Briquel, J. Mazzolini, T. Le Bris, O. Boyron, F. Boisson, F. Delolme, F. D'Agosto, C. Boisson, R. Spitz, *Angew. Chem. Int. Ed.* **2008**, *47*, 9311 – 9313; *Angew. Chem.* **2008**, *120*, 9451 – 9453; g) R. Godoy Lopez, F. D'Agosto, C. Boisson, *Prog. Polym. Sci.* **2007**, *32*, 419 – 454; h) R. Godoy Lopez, C. Boisson, F. D'Agosto, R. Spitz, F. Boisson, D. Gigmes, D. E. Bertin, *Macromol. Rapid Commun.* **2006**, *27*, 173 – 181; i) R. Godoy Lopez, C. Boisson, F. D'Agosto, R. Spitz, F. Boisson, D. Bertin, P. Tordo, *Macromolecules* **2004**, *37*, 3540 – 3542.

[11] I. German, W. Kelhifi, S. Norsic, C. Boisson, F. D'Agosto, *Angew. Chem. Int. Ed.* **2013**, *52*, 3438 – 3441; *Angew. Chem.* **2013**, *125*, 3522 – 3525.

[12] H. Makio, T. Ochiai, J. Mohri, K. Takeda, T. Shimazaki, Y. Usui, S. Matsuura, T. Fujita, *J. Am. Chem. Soc.* **2013**, *135*, 8177 – 8180.

[13] a) H. Terao, S. Ishii, J. Saito, S. Matsuura, M. Mitani, N. Nagai, H. Tanaka, T. Fujita, *Macromolecules* **2006**, *39*, 8584 – 8593; b) A. V. Sesha Sainath, M. Isokawa, M. Suzuki, S. Ishii, S. Matsuura, N. Nagai, T. Fujita, *Macromolecules* **2009**, *42*, 4356 – 4358; c) H. Makio, T. Fujita, *Acc. Chem. Res.* **2009**, *42*, 1532 – 1544; d) K. Matoishi, K. Nakai, N. Nagai, H. Terao, T. Fujita, *Catal. Today* **2011**, *164*, 2 – 8; e) S. Ishii, M. Mitani, J. Saito, S. Matsuura, S. Kojoh, N. Kashiwa, T. Fujita, *Chem. Lett.* **2002**, 740 – 741; f) R. Mülhaupt, T. Duschek, B. Rieger, *Makromol. Chem. Macromol. Symp.* **1991**, *48 – 49*, 317 – 332.

[14] a) J. Mazzolini, O. Boyron, V. Monteil, D. Gigmes, D. Bertin, F. D'Agosto, C. Boisson, *Macromolecules* **2011**, *44*, 3381 – 3387; b) Y. Zhang, H. Li, J.-Y. Dong, Y. Hu, *Polym. Chem.* **2014**, *5*, 105 – 115; c) Y. Zhang, H. Li, Y. Zhang, Q. Li, Z. Ma, J.-Y. Dong, Y. Hu, *Macromol. Chem. Phys.* **2014**, *215*, 763 – 775.

[15] A. B. Lowe, *Polym. Chem.* **2014**, *5*, 4820 – 4870.

[16] V. B. Patil, K. O. Saliu, R. M. Jenkins, E. M. Carnahan, E. J. Kramer, G. H. Fredrickson, G. C. Bazan, *Macromol. Chem. Phys.* **2014**, *215*, 1140 – 1145.

[17] F. Lucas, F. Peruch, S. Carlotti, A. Deffieux, A. Leblanc, C. Boisson, *Polymer* **2008**, *49*, 4935 – 4941.

[18] T. Shiono, N. Naga, K. Soga, *Makromol. Chem. Rapid Commun.* **1993**, *14*, 323 – 327.

[19] a) L. M. Pitet, M. A. Amendt, M. A. Hillmyer, *J. Am. Chem. Soc.* **2010**, *132*, 8230 – 8231; b) K. Sill, T. Emrick, *J. Polym. Sci. Part A* **2005**, *43*, 5429 – 5439.

[20] a) Z. Xu, S. Jie, B.-G. Li, *J. Polym. Sci. Part A* **2014**, *52*, 3305; b) S. S. Sengupta, J. S. Parent, *Polym. Eng. Sci.* **2006**, *46*, 480 – 485; c) J. S. Parent, S. S. Sengupta, *Macromolecules* **2005**, *38*, 5538 – 5544.

[21] a) C. J. Han, M. S. Lee, D.-J. Byun, S. Y. Kim, *Macromolecules* **2002**, *35*, 8923 – 8925; b) H. Kaneyoshi, Y. Inoue, K. Matyjaszewski, *Macromolecules* **2005**, *38*, 5425 – 5435; c) S. K. T. Pillai, W. P. Kretschmer, M. Trebbin, S. Förster, R. Kempe, *Chem. Eur. J.* **2012**, *18*, 13974 – 13978.

[22] a) A. J. D. Magenau, J. W. Chan, C. E. Hoyle, R. F. Storey, *Polym. Chem.* **2010**, *1*, 831 – 833; b) J. Mazzolini, I. Mokthari, R. Briquet, O. Boyron, F. Delolme, V. Monteil, D. Bertin, D. Gigmes, F. D'Agosto, C. Boisson, *Macromolecules* **2010**, *43*, 7495 – 7503.

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