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Controlled Radical Polymerization of Ethylene Using Organotellurium Compounds

Yasuyuki Nakamura[a], Bastian Ebeling[b], Arne Wolpers[b], Vincent Monteil*[b], Franck D’Agosto*[b], and Shigeru Yamago*[a]

Abstract: The first successfully controlled radical polymerization (CRP) of ethylene is reported using several organotellurium chain-transfer agents (CTAs) under mild conditions (70 °C, 200 bar of ethylene) within the concept of organotellurium-mediated radical polymerization (TERP). In contrast to preceding works on CRPs of ethylene applying reversible addition–fragmentation chain-transfer (RAFT), the TERP system provided a high livingness and chain-end functionalization of polyethylene chains. Molar-mass distributions with dispersities between 1.3 and 2.1 were obtained up to average molar masses of 5000 g mol^{-1}. As in the RAFT system, the high reactivity of the growing polyethylenyl radical led to an inherent side reaction. For the presented TERP systems, however, this side reaction did not result in dead chains, while it could even be effectively suppressed by a good choice of the CTA.

Polyethylene (PE) is one of the most widely used plastics in the world and is industrially produced from ethylene by radical polymerizations giving more branched low-density PE or by coordination polymerizations giving less branched high-density PE.[1–4] Prospectively, the macromolecular engineering of PE through the control of its primary structure (i.e., characteristics such as average molar mass, molar-mass distribution (MMD),[5–8] branching density, and the introduction of functional groups[9–13]) is expected to fabricate new polyolefin-based high value-added materials. The development of new catalysts for coordination polymerizations led to significant advances for high-density PE synthesis, enabling living polymerizations, end-group functionalities, and copolymerization with polar monomers. In contrast, similar advances for low-density PE remain a formidable challenge, despite the continuous developments in the field of controlled radical polymerizations (CRPs, or reversible-deactivation radical polymerizations, RDRPs).

Among the most widely used CRP methods are the nitroxide-mediated radical polymerization (NMP),[14] the atom-transfer radical polymerization (ATRP),[15,16] and the reversible addition–fragmentation chain transfer (RAFT) polymerization,[17] while more recent methods are the organotellurium-mediated radical polymerization (TERP)[18] and the cobalt-mediated radical polymerization (CMRP).[19] CRPs under NMP, ATRP, RAFT, and TERP conditions are well-established for *conjugated* monomers, and several resulting polymer products have already been commercialized.[20] The applicability for *unconjugated* monomers, however, is limited and CRPs of *N*-vinylamides or vinyl acetate for example are only possible via RAFT,[21] TERP,[22] or CMRP.[23] CRP of ethylene has not even been promisingly approached until very recently, which will be addressed in more detail in the next paragraph. This is mainly due to two reasons: (1) As the polyethylenyl radical is unconjugated and does not bear any stabilizing groups, the reversible activation of the dormant (reversibly deactivated) polymer species, which is essential for CRPs, does not occur readily. (2) Many CRP systems and their experimental setups are incompatible with the high temperatures (200–300 °C) and pressures (1000–4000 bar) conventionally believed to be necessary for an effective radical polymerization of ethylene.[24–26]

Providing a basis for the present study, in 2009, one of the authors revisited milder conditions for ethylene radical polymerizations and demonstrated that they can be effective also at < 80 °C and < 250 bar if the solvent system is chosen wisely.[27–29] These conditions were subsequently applied using RAFT with xanthates as chain-transfer agents (CTAs), which yielded the first radical polymerization of ethylene with chain-growth-controlled characteristics.[30] However, despite dispersities $Đ$ (= M_w/M_n ; M_w: weight-average molar mass, M_n: number-average molar mass) lower than 1.5 up to M_n values of 1500 g mol^{-1}—corresponding to an average degree of polymerization of about 50—the system suffered from an inherent side reaction. As shown in Scheme 1a, the key mechanism in RAFT polymerizations is the degenerative chain transfer (DT) with an equilibrium between a polyethylenyl radical $P^{\bullet}$ or $P'^{\bullet}$ and a PE–xanthate dormant species **1** or **1’** through the intermediate radical **2**. For PE, **2** can undergo fragmentation giving radical $R^{\bullet}$ and polymer **3** that features two chains bound by one SC(=O)S bridge, which is due to the similar stability between $R^{\bullet}$ for R = Me, Et and a polyethylenyl radical. As the C=O double bond in **3** is much less reactive toward radical addition than the C=S double bond in **1** or **1’**, **3** is virtually dead and accumulates in the system, diminishing its chain-growth control.

Another of the authors developed TERP[18,31–33] with features such as high monomer versatility,[34–37] high compatibility with functional groups,[38] as well as high flexibility in copolymer synthesis[39] and polymer chain-end modifications.[40–42] Whereas TERP mainly proceeds by the DT mechanism like RAFT (Scheme 1b),[32] it does not involve a stable intermediate radical during the DT process.[18] As TERP shows a better control in

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[a] Dr. Y. Nakamura, Prof. Dr. S. Yamago
Institute for Chemical Research, Kyoto University, Gokasyo, Uji, Kyoto 611-0011, Japan
E-mail: yamago@scl.kyoto-u.ac.jp
[b] Dr. B. Ebeling, Dr. A. Wolpers, Dr. V. Monteil, Dr. F. D’Agosto
Université de Lyon, Université Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire C2P2, Équipe LCPP, 69616 Villeurbanne CEDEX, France
E-mail: vincent.monteil@univ-lyon1.fr
franck.dagosto@univ-lyon1.fr

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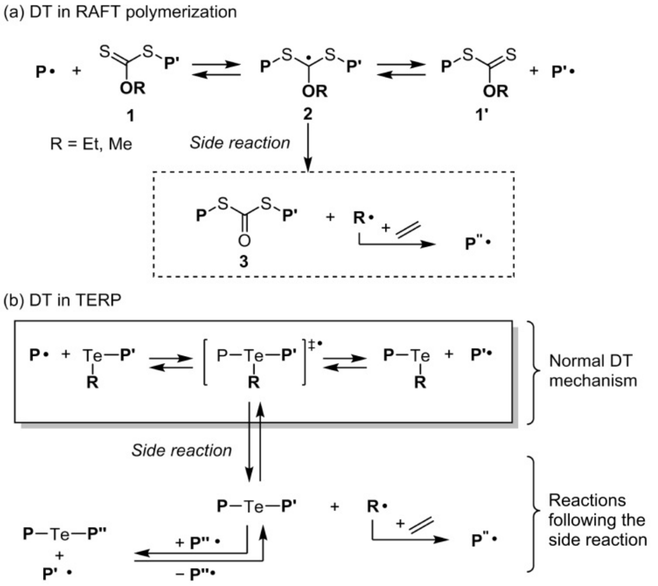
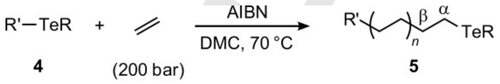


Scheme 1. (a) Degenerative chain transfer (DT) for RAFT and the side reaction observed in the polymerization of ethylene.[30] (b) DT in TERP. P, P', and P'' denote polymer chains.

copolymerizations of 1-alkenes and acrylates[35,36] than RAFT,[43–45] it is an excellent candidate for a CRP of ethylene. In addition, as it is presented in Scheme 1b, although the R group in the DT of TERP may be liberated in a side reaction similar to the one in the RAFT system, the chemical nature of the resulting organotellurium compound P–Te–P' indicates that it might still serve as an effective CTA, preventing the accumulation of dead chains. In the present communication, we report the first TERP of ethylene. With an appropriate design of the CTAs, CRPs proceeded successfully giving PE with M_w/M_n values between 1.3 and 2.1 up to M_n = 5000 g mol^{-1}.

The experimental setup and conditions used for TERPs of ethylene were similar to the ones used in the preceding work on RAFT polymerizations.[30] In a typical polymerization procedure, the radical initiator 2,2'-azobis(2-methylpropionitrile) (AIBN, 50 mg, 6.09 mmol L^{-1}) and an organotellurium CTA (18.3 mmol L^{-1}, 3 equiv with respect to AIBN) were stirred in dimethyl carbonate (DMC) in an autoclave reactor under 200 bar of ethylene pressure at 70 °C. The starting mixture was homogeneous and turned to a suspension upon ethylene consumption. The resulting yield of PE was determined gravimetrically while the product was analyzed via size-exclusion chromatography (SEC) and NMR. The used substances, the experimental setup, the polymerization procedure, and the analytical methods are more thoroughly described in the Supporting Information.

Showing excellent control in polymerizations of conjugated monomers and *N*-vinyl amides,[33,47] **4a** (see Scheme 2) was selected as first potential CTA. After 3 h, 2.10 g of product were collected, resulting in 1.76 g of ethylene conversion (Table 1, run 1). SEC analysis gave an MMD with M_w/M_n = 1.31 and M_n(SEC) = 2100 g mol^{-1} close to the M_n value theoretically expected according to the principles of CRPs, M_n(theo) = 2200 g mol^{-1}. The influence of **4a** was significant, as a polymerization without **4a** under otherwise identical conditions gave PE with M_n(SEC) = 14 000 g mol^{-1} and M_w/M_n = 3.4, while the ethylene conversion was slightly higher (2.04 g, run 2).



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a: R' = C(CO$_2$Et)Me$_2$, R = Ph
b: R' = C(CO$_2$Et)Me$_2$, R = Me
c: R' = R = Bu
d: R' = C(CN)Me$_2$, R = Ph
e: R' = CH(CO$_2$Bu)Me, R = Me
f: R' = CHMe$_2$, R = Ph
g: R' = Bu, R = Ph

Scheme 2. TERPs of ethylene in the presence of CTAs **4a–g**. The notations α and β indicate the position of CH$_2$ in relation to the Te atom.

Additional polymerizations with **4a** were conducted for 1 h (run 3), 6 h (run 4), and 17 h (run 5). Ethylene conversion increased with reaction time, while the M_n(SEC) values increased linearly with conversion, being generally close to the respective M_n(theo) value (Figure 1), supporting the role of 4a as an effective CTA. The initially narrower MMDs with M_w/M_n < 1.4 broadened during the course of polymerization up to M_w/M_n = 2.1, while the M_n(SEC) values tend to get a slight downward deviation from M_n(theo), which was mainly assigned to the inevitable continuous initiation of new chains by AIBN.

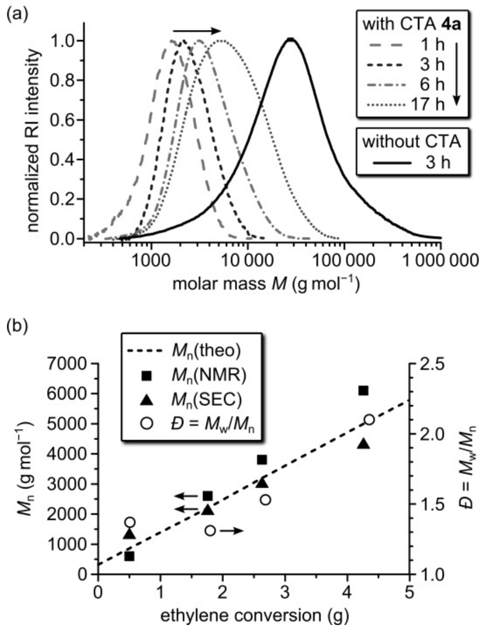

Figure 1. (a) MMDs (SEC traces) of PE prepared in the presence of CTA **4a** (Table 1, runs 1, 3–5) and without CTA (run 2), and (b) M_n and M_w/M_n values versus ethylene conversion for the system with CTA **4a**.

Table 1. Radical polymerization of ethylene in the presence of organotellurium CTAs (Scheme 2).[a]

Run	CTA	Time (h)	Ethylene conversion[b] (g)	M_n(theo)[c] (g mol^{-1})	M_n(SEC)[d] (g mol^{-1})	M_n(NMR)[e] (g mol^{-1})	M_w/M_n[d]	**5/6**[f]
1	**4a**	3	1.76	2200	2100	2600	1.31	>99/<1
2	None	3	2.04	–	14 000	–	3.4	–
3	**4a**	1	0.50	860	1300	600	1.37	>99/<1
4	**4a**	6	2.63	3200	3000	3800	1.53	99/1
5	**4a**	17	4.26	5000	4300	6100	2.1	97/3
6	**4a**[g]	3	1.29	740	650	630	1.50	>99/<1
7	**5a**[h]	6	2.51	3500	3400	4500	1.75	99/1
8	**4b**	1	0.20	480	830	830	1.57	84/16
9	**4b**	3	1.90	2300	2200	2900	1.44	33/67
10	**4b**	6	3.48	4100	2900	4900	1.74	9/91
11	**4c**	1	1.00	1300	1100	–[i]	1.59	–[j]
12	**4c**	3	2.65	3100	2000	–[i]	1.90	–[j]
13	**4d**	3	0.89	1300	1500	–[i]	1.36	>99/<1
14	**4e**	3	2.28	2800	2400	3000	1.47	25/75
15	**4f**	3	2.08	2500	2100	–[i]	1.40	96/4
16	**4g**	1	0.63	950	1200	–[i]	1.59	99/1
17	**4g**	3	1.70	2100	2000	–[i]	1.52	97/3

[a] AIBN (6.09 mmol L^{-1}), CTA (18.3 mmol L^{-1}, 3 equiv with respect to AIBN) in DMC (50 mL) under ethylene (200 bar) at 70 °C. [b] Ethylene conversion (g) = (mass of dried product (g)) – (mass of AIBN (g)) – (mass of CTA (g)). [c] M_n(theo) (g mol^{-1}) = (ethylene conversion (g))/(amount of CTA (mol)) + (molar mass of CTA (g mol^{-1})). [d] Determined by SEC. [e] Calculated by comparing the ^{1}H NMR signals of the PE chain and of the R' end-group. [f] Ratio in mol/mol determined by ^{1}H NMR from α-CH$_2$ group of **5** and α-CH$_2$ group of **6**. [g] 10 equiv of CTA with respect to AIBN. [h] CTA is the dried product of run 6. [i] No distinct ^{1}H NMR signal of the R'-group. [j] ^{1}H NMR signals of species **5c** and **6** too similar for a precise mathematical distinction (Figure S3).

In fact, while M_n(theo) = 5000 g mol^{-1} for PE after 17 h, a rough estimation that takes into account the number of chains initiated by AIBN[48,49,50] (see Supporting Information) gives an expected M_n value of 4400 g mol^{-1}, being close to the actually obtained M_n(SEC) = 4300 g mol^{-1}.

The livingness of PE chains end-capped with a TePh group (**5a**) was shown in a chain-extension experiment (run 7, see Supporting Information) and via ^{1}H NMR analysis. A thorough NMR analysis of PE generated in the presence of **4a** will be exemplarily given in the following.

Figure 2a depicts the ^{1}H NMR spectrum of PE produced in run 1. The intense signal at 1.25 ppm and the broad signal at 0.85 ppm correspond to the CH$_2$ repeating unit and CH$_3$ chain ends, respectively. The latter is the result of an unavoidable formation of branches due to intramolecular chain transfer.[51] The remaining signals were assigned to the expected α-chain-end, i.e., the ester group C(CO$_2$Et)Me$_2$ (signals a–c), and the expected ω-chain-end, i.e., the phenyltellanyl group TePh (signals d–h). The M_n value determined from the integration of the α-polymer chain end (signal a) and the CH$_2$ repeating unit

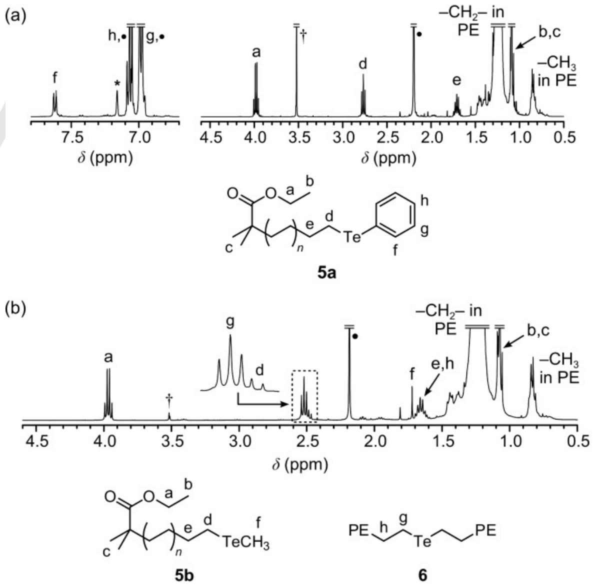

Figure 2. ^{1}H NMR spectra of PE synthesized (a) in the presence of **4a** (Table 1, run 1) and (b) the presence of **4b** (run 9); * NMR solvent benzene, † polymerization solvent DMC, • collecting solvent toluene.

(hypothetically assuming 100% of living chains initiated by the R'-group), M_n(NMR) = 2600 g mol^{-1}, was in good agreement with M_n(theo) = 2200 g mol^{-1} and M_n(SEC) = 2100 g mol^{-1}. The extent of the above-mentioned branching was calculated via ^{13}C NMR, which is more thoroughly described in the Supporting Information.[50] The impact of **4a** is small as the determined 4.1 branches per 1000 carbon atoms are close to the 4.7 branches calculated for the CTA-free system of run 2.

In the ^{1}H NMR spectra of the PE samples prepared for longer polymerization times (6 h and 17 h), a weak triplet signal was observed at 2.53 ppm (data not shown). It was assigned to the α-CH2 protons of species **6** (Figure 3), indicating the side reaction presented in Scheme 1b (with R = Ph). By comparing this signal with signal d of the expected species **5a** (cf. Figure 2a), the formation of **6** was estimated to be < 1% after 1 h and 3 h, 1% after 6 h, and 3% after 17 h. As it was for the RAFT system, this is the first observation of such a fragmentation of the R group for TERP and can be attributed to the relative stability of the bonds between the Te atom and either the polymer chain or the R group. Theoretical calculations of the C–Te dissociation energies of the molecule Et–Te–Ph (simulating **5a**/PE–Te–Ph) gave 187 kJ/mol for the Et–Te bond and 242 kJ/mol for the Te–Ph bond (Figure S3). The difference of 55 kJ/mol is much smaller than the ones usually expected for bonds of Te with polymer chains derived from *conjugated* monomers and with Ph groups (> 100 kJ/mol),[18] which explains why the fragmentation over the Ph radical is that pronounced in ethylene polymerization.

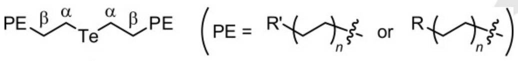

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Figure 3. Species **6** formed after the side reaction depicted in Scheme 1b.

To further investigate the effect of side-fragmentation, polymerizations were conducted with the Me-substituted CTA **4b** (R = Me). Theoretical calculations (Figure S3) of the bond dissociation energies of the model compound Et–Te–Me gave a much smaller difference of 19 kJ/mol (198 kJ/mol and 217 kJ/mol for the Et–Te and Te–Me bond, respectively), so that more frequent fragmentation over the Me group should be observed compared to the Ph group. For 1 h, 3 h, and 6 h (run 8, 9, and 10, respectively), the same polymerization conditions were applied as for **4a**. Judging from the comparison of the ^{1}H NMR signals d and g (Figure 2b, exemplarily given for PE after 3 h), the amount of **6** increased rapidly in the course of the polymerization from 16% after 1 h over 67% after 3 h to 91% after 6 h. Nevertheless, the system still preserves chain-growth control, as M_n(SEC) values increase with increasing ethylene conversion with only slightly higher M_w/M_n than for **4a** (a more thorough discussion of the obtained MMDs is presented below). Polymerization rates were again close to the CTA-free system. As the structural difference between **6** and **5b** is not very big (PE–Te–PE vs. PE–Te–Me), it can be expected that **6** is indeed far from being a dead polymer species—as **3** is for RAFT. To test into that, Bu–Te–Bu (Bu: *n*-butyl, **4c**), which simulates species **6**, was used as potential CTA. Polymerizations were conducted for 1 h and 3 h (Table 1, run 11 and 12, respectively) under the standard conditions. The resulting M_n(SEC) values increased with increasing ethylene conversion and were far from the ones of the CTA-free system. The obtained M_w/M_n values were only slightly higher than the ones obtained for the polymerization with CTA **4b**. ^{1}H NMR spectra showed the formation of both PE–Te–Bu (**5c**) and **6** after the release of either one or both butyl groups for (re)initiation of chains (Figure S4), which supports that **4c** and thus **6** works as an effective CTA. It should be mentioned that for the polymerization time of 3 h, there is a distinct downward deviation of M_n(SEC) from M_n(theo) with an increase of M_w/M_n, which is expected to originate from a Te–C bond cleavage of the obtained PE during the SEC experiment at 150 °C. This cleavage has a higher impact on SEC results of PE with more **6**, as it separates two long PE chains in this case (see also run 10). A more thorough discussion of this effect is given in the Supporting Information.

Although the formation of **6** has no drastically detrimental effect on the general chain-growth control itself, it has consequences that are often undesired in CRPs. **6** is a polymer species that is statistically twice as long as the ones it originates from (PE–Te–PE from PE–TeR + PE macroradical), resulting in a mixture of single- and double-chain species broadening the obtained total MMD. In addition, processing of the polymeric product exploiting the Te end-group is expected to be more challenging, as **6** has (i) only one functional Te atom/group for two PE chains (ii) located in the middle of the macromolecule. This clarifies the necessity to avoid the formation of **6** by a good choice of the R group for most cases. In the context of the present work, it can generally be expected that the Ph-substituted CTA would lead to a better MMD control than the Me derivative (or PE derivatives like **6**), as organotellurium CTAs carrying a Ph group have a higher chain-transfer rate than those carrying a Me group for polystyrene.[46]

Under the standard conditions, CTAs with different R'-groups of decreasing activity were investigated: C(CN)Me$_2$ (**4d**, run 15) > CH(CO$_2$Bu)Me (**4e**, run 16) > CHMe$_2$ (**4f**, run 17) > Bu (**4g**, runs 18 and 19). In all cases, CRPs were obtained with M_n(SEC) values close to M_n(theo). The slight tendency of lower M_w/M_n values can be observed for CTAs with more activated R'-groups, potentially indicating benefits from a faster deactivation of the PE macroradical. Differences in polymerization rates might be attributed to different (re)initiation rates of the respective R'$^\bullet$ radicals.

In conclusion, CRPs of ethylene were successfully conducted by TERP, while the impact of the CTA's structure on the generated PE is well-understood. After the pioneering work on RAFT polymerizations, the here presented system finally allows high end-functionality and livingness of chains and is thus a game changer in terms of control and further processing of PE. It lays the foundation of more complex and feasible molecular architectures and sophisticated polyolefin-based materials.

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Keywords: polyethylene • polymerization • TERP • tellurium • controlled-radical polymerization

[1] M. P. McDaniel, *Adv. Catal.* **2010**, *53*, 123–606.
[2] M. C. Baier, M. A. Zuideveld, S. Mecking, *Angew. Chem. Int. Ed.* **2014**, *53*, 9722–9744.
[3] M. Stürzel, S. Mihan, R. Mülhaupt, *Chem. Rev.* **2015**, *116*, 1398–1433.
[4] P. D. Hustad, *Science* **2009**, *325*, 704–707.
[5] L. R. Sita, *Angew. Chem. Int. Ed.* **2009**, *48*, 2464–2472.
[6] F. Alfano, H. W. Boone, V. Busico, R. Cipullo, J. C. Stevens, *Macromolecules* **2007**, *40*, 7736–7738.
[7] R. Kempe, *Chem. Eur. J.* **2007**, *13*, 2764–2773.
[8] D. J. Arriola, E. M. Carnahan, P. D. Hustad, R. L. Kuhlman, T. T. Wenzel, *Science* **2006**, *312*, 714–719.
[9] A. Berkefeld, S. Mecking, *Angew. Chem. Int. Ed.* **2008**, *47*, 2538–2542.
[10] T. S. Thomas, W. Hwang, L. R. Sita, *Angew. Chem. Int. Ed.* **2016**, *55*, 4683–4687.
[11] S. Norsic, C. Thomas, F. D'Agosto, C. Boisson, *Angew. Chem. Int. Ed.* **2015**, *54*, 4631–4635.
[12] 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.
[13] I. German, W. Kelhifi, S. Norsic, C. Boisson, F. D'Agosto, *Angew. Chem. Int. Ed.* **2013**, *52*, 3438–3441.
[14] J. Nicolas, Y. Guillaneuf, C. Lefay, D. Bertin, D. Gigmes, B. Charleux, *Prog. Polym. Sci.* **2013**, *38*, 63–235.
[15] M. Ouchi, T. Terashima, M. Sawamoto, *Chem. Rev.* **2009**, *109*, 4963–5050.
[16] K. Matyjaszewski, N. V. Tsarevsky, *Nat. Chem.* **2009**, *1*, 276–288.
[17] G. Moad, E. Rizzardo, S. H. Thang, *Aust. J. Chem.* **2012**, *65*, 985–1076.
[18] S. Yamago, *Chem. Rev.* **2009**, *109*, 5051–5068.
[19] A. Debuigne, C. Jérôme, C. Detrembleur, *Polymer* **2017**, *115*, 285–307.
[20] M. Destarac, *Macromol. React. Eng.* **2010**, *4*, 165–179.
[21] M. H. Stenzel, L. Cummins, G. E. Roberts, T. P. Davis, P. Vana, C. Barner-Kowollik, *Macromol. Chem. Phys.* **2003**, *204*, 1160–1168.
[22] Y. Kwak, A. Goto, T. Fukuda, Y. Kobayashi, S. Yamago, *Macromolecules* **2006**, *39*, 4671–4679.
[23] A. Kermagoret, C.-A. Fustin, M. Bourguignon, C. Detrembleur, C. Jérôme, A. Debuigne, *Polym. Chem.* **2013**, *4*, 2575–2583.
[24] K. W. Doak in *Encyclopedia of Polymer Science and Engineering, 2nd ed., Vol. 6* (Eds.: H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges), Wiley Interscience, New York, **1985**, pp. 386–428.
[25] S. L. Aggarwal, O. J. Sweeting, *Chem. Rev.* **1957**, *57*, 665–742.
[26] J. Merna, P. Vlček, V. Volkis, J. Michl, *Chem. Rev.* **2016**, *116*, 771–785.
[27] E. Grau, J.-P. Broyer, C. Boisson, R. Spitz, V. Monteil, *Macromolecules* **2009**, *42*, 7279–7281.
[28] E. Grau, J.-P. Broyer, C. Boisson, R. Spitz, V. Monteil, *Polym. Chem.* **2011**, *2*, 2328–2333.
[29] E. Grau, J.-P. Broyer, C. Boisson, R. Spitz, V. Monteil, *Phys. Chem. Chem. Phys.* **2010**, *12*, 11665–11669.
[30] C. Dommanget, F. D'Agosto, V. Monteil, *Angew. Chem. Int. Ed.* **2014**, *53*, 6683–6686.
[31] S. Yamago, K. Iida, J. Yoshida, *J. Am. Chem. Soc.* **2002**, *124*, 2874–2875.
[32] A. Goto, Y. Kwak, T. Fukuda, S. Yamago, K. Iida, M. Nakajima, J. Yoshida, *J. Am. Chem. Soc.* **2003**, *125*, 8720–8721.
[33] S. Yamago, Y. Ukai, A. Matsumoto, Y. Nakamura, *J. Am. Chem. Soc.* **2009**, *131*, 2100–2101.
[34] E. Mishima, S. Yamago, *Macromol. Rapid Commun.* **2011**, *32*, 893–898.
[35] E. Mishima, T. Tamura, S. Yamago, *Macromolecules* **2012**, *45*, 2989–2994.
[36] E. Mishima, T. Tamura, S. Yamago, *Macromolecules* **2012**, *45*, 8998–9003.
[37] E. Mishima, S. Yamago, *J. Polym. Sci. A Polym. Chem.* **2012**, *50*, 2254–2264.
[38] Y. Nakamura, M. Yu, Y. Ukai, S. Yamago, *ACS Sym. Ser.* **2015**, *1187*, 295–309.
[39] S. Yamago, K. Iida, J. Yoshida, *J. Am. Chem. Soc.* **2002**, *124*, 13666–13667.
[40] T. Yamada, E. Mishima, K. Ueki, S. Yamago, *Chem. Lett.* **2008**, 650–651.
[41] E. Kayahara, H. Yamada, S. Yamago, *Chem. Eur. J.* **2011**, *17*, 5271–5279.
[42] Y. Nakamura, T. Arima, S. Yamago, *Macromolecules* **2014**, *47*, 582–588.
[43] S. Liu, A. Sen, *J. Polym. Sci. A Polym. Chem.* **2004**, *42*, 6175–6192.
[44] S. Liu, B. Gu, H. A. Rowlands, A. Sen, *Macromolecules* **2004**, *37*, 7924–7929.
[45] R. Venkatesh, B. B. P. Staal, B. Klumperman, *Chem. Commun.* **2004**, 1554–1555.
[46] E. Kayahara, S. Yamago, Y. Kwak, A. Goto, T. Fukuda, *Macromolecules* **2008**, *41*, 527–529.
[47] K. Nakabayashi, H. Mori, *Eur. Polym. J.* **2013**, *49*, 2808–2838.
[48] M. J. Monteiro, *J. Polym. Sci. A Polym. Chem.* **2005**, *43*, 3189–3204.
[49] Z. Guan, J. R. Combes, Y. Z. Menceloglu, J. M. Desimone, *Macromolecules* **1993**, *26*, 2663–2669.
[50] Y. Nakamura, Y. Kitada, B. Ray, S. Yamago, *Macromolecules*, **2011**, *44*, 8388-8397.
[51] G. B. Galland, R. F. de Souza, R. S. Mauler, F. F. Nunes, *Macromolecules* **1999**, *32*, 1620–1625.

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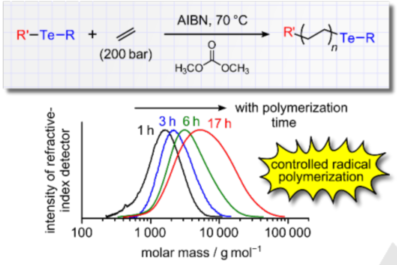
Layout 1:

COMMUNICATION

Organotellurium-mediated radical polymerizations (TERPs) of ethylene were conducted under rather mild conditions (70 °C, 200 bar). In addition to the good chain-growth control, high functionality of the polyethylene chain-ends was obtained for the first time, finally fixing a crippling problem of controlled radical polymerizations of ethylene. AIBN = 2,2'-azobis(2-methylpropionitrile).



Yasuyuki Nakamura, Bastian Ebeling, Arne Wolpers, Vincent Monteil, Franck D'Agosto*, Shigeru Yamago**

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