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Polymerization of Ethylene through Reversible Addition–Fragmentation Chain Transfer (RAFT)**

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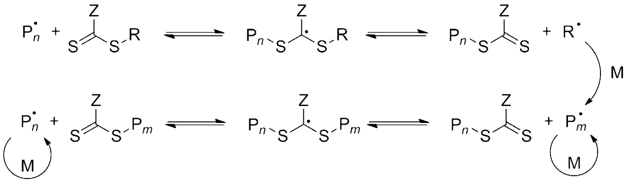
Abstract: *The present paper reports the first example of a controlled radical polymerization of ethylene using reversible addition–fragmentation chain transfer (RAFT) in the presence of xanthates (Alkyl-OC(=S)S-R) as controlling agents under relative mild conditions (70°C, <200 bars). The specific reactivity of the produced alkyl-type propagating radicals induces a side fragmentation reaction of the stabilizing O-alkyl Z group of the controlling agents. This fragmentation, rarely observed in RAFT, was proven by NMR analyses. In addition, semicrystalline copolymers of ethylene and vinyl acetate were also prepared with a similar level of control.*

The tremendous amount and broad utility of polyolefins are related to the possibility to prepare many different kinds of materials from a very simple set of inexpensive building blocks (ethylene, propylene, and higher α-olefins).[1] Ethylene, the simplest and cheapest available olefin, is an extremely attractive monomer with a feedstock that can be independent from oil production and obtained by biological resources.[2] Polyethylene is industrially obtained through catalytic coordination insertion (Ziegler–Natta[3] or Phillips[4] catalysis) or free-radical polymerizations.[5]

Controlling the growth of the chains during a polymerization process enables the fine-tuning of the properties of the final material, for example by reaching block copolymer structures. In the field of catalytic polymerization, coordinative chain-transfer polymerization (CCTP)[6] is the only industrially relevant system to produce olefin block copolymers (OBC).[7] So far however, this technique is limited to apolar olefin polymers. To introduce polar groups into polyolefins, industry resorts to free-radical chemistry, either by copolymerizing olefins with polar monomers (e.g. copolymers of ethylene and vinyl acetate, also called EVA)[5] or by postmodification of a preformed polyolefin.[8] However, the conditions required are too harsh (temperature up to 300°C and pressure up to 3000 bars) to control the macromolecular architecture.[9] In this context, identifying original ways to polymerize ethylene under conditions that allow the fine-control of the chain growth through a free-radical process is very appealing.

The advent of reversible deactivation radical polymerizations (RDRP), also called controlled radical polymerizations (CRP), has revolutionized macromolecular chemistry during these last two decades. CRP techniques are either based on a reversible termination (ATRP,[10] NMP,[11] OMRP[12]) or a reversible transfer reaction (RAFT).[13] Despite its success for the majority of polymerizable monomers, CRP still suffers from limitations. The copolymerization of ethylene and α-olefins with polar monomers such as (meth)acrylates has been achieved through CRP,[14] but only low olefin contents were obtained. Recently, Debuigne and Detrembleur[15] synthesized amorphous copolymers of vinyl acetate, acrylonitrile, or *N*-methyl vinyl acetamide with ethylene (ethylene molar content lower than 55%) using cobalt-mediated radical polymerization. Ethylene remains a challenging monomer for CRP. Herein, we report that RAFT polymerization of ethylene meets the requirements of a CRP.

Indeed, RAFT is probably the most versatile process to achieve the control of the polymerization of both activated monomers (such as styrenic or (meth)acrylic types) and less activated monomers (such as vinyl acetate, *N*-vinyl pyrrolidone, *N*-vinyl carbazole).[16] The control is established by the use of thiothiocarbonylated compounds (ZC(=S)SR such as trithiocarbonate (Z = −S-alkyl), dithioester (Z = −R′), xanthate (Z = −OR′), or dithiocarbamate (Z = −NR′$_2$)) mediating an equilibrium between dormant and active chains according to a reversible transfer reaction (Scheme 1). When the leaving radical $P_n^{\bullet}$ is not sufficiently stabilized, such as those obtained during the polymerization of less activated monomers, dithioesters or trithiocarbonates inhibit the polymerization with respect to the R fragment of the



Scheme 1. Activation/deactivation (pre)equilibrium in RAFT polymerization. P_n and P_m denote growing macroradicals of polymerization degree of *n* and *m*, respectively, M = monomer.

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controlling agent. Xanthate proved to be extremely efficient to control the polymerization in these cases (the process is also called macromolecular design by interchange of xanthates, MADIX).[17] Considering ethylene as a non-activated monomer, we took advantage of our recent progress in efficiently performing the free-radical polymerization of ethylene under mild conditions ($T < 100$ °C, $P < 300$ bars)[18–20] to investigate the RAFT polymerization of ethylene mediated by xanthates. To the best of our knowledge, this has never been done before.

In our previous studies on the free-radical polymerization of ethylene,[18–20] we demonstrated that it was crucial to use dimethylcarbonate (DMC) as solvent in order to minimize irreversible chain-transfer reactions and to guarantee high productivity. RAFT polymerizations were thus performed in dichloromethane (DMC) at 200 bars and 70 °C. Under these conditions, *O*-ethyl xanthate **1** (Figure 1) was first selected to mediate the RAFT polymerization of ethylene in the presence of 2,2′-azobisisobutyronitrile (AIBN) as initiator.

Figure 1. Xanthates used in the ethylene RAFT polymerizations performed in this study.

The ratio of **1**/AIBN was fixed to 10:1. As the sampling was not possible during the polymerization, the kinetics were followed by performing discrete experiments for different times (from 1 h to 7 h). At the end of each experiment, the polymer was recovered, weighed, and characterized by high-temperature size-exclusion chromatography (SEC) and nuclear magnetic resonance (NMR)spectroscopy. These experiments were compared to blank experiments performed in the absence of **1** (see the Supporting Information, Table S1). No significant impact of the presence of **1** on the yield of the polymer was observed. In addition, the number-average molar masses (M_n) obtained for the experiments performed in the absence of **1** seemed to be almost constant and broadly distributed (dispersity $Đ$ up to 10). For the RAFT polymerization mediated by **1**, a linear increase of M_n versus the yield was observed (Figure 2) and much narrower molar mass distributions were obtained. Indeed, dispersities decreased from 2.0 (after 1 h of polymerization) to 1.4 (after 3 h) and increased again to 1.9 (after 7 h). Eventually, an excellent agreement was observed between the theoretical and experimental M_n, although a slight broadening of the peaks occurred after 4 h of polymerization, consistent with the observed increase of $Đ$. These data show that the polymerization of ethylene is controlled by **1** according to a RAFT process.

The polyethylene obtained after 7 h of polymerization was further characterized by differential scanning calorimetry (DSC) and showed a melting temperature of 116 °C (crystallinity of 50 %). It exhibits a slightly higher melting temperature (and crystallinity) than a low-density polyethylene (obtained by free-radical polymerization at high temperature and at very high pressure), corresponding to a less branched structure consistent with ^{13}C NMR analyses (see the Supporting Information, Figure S3; 3.7 branches/1000 C atoms for the polyethylene obtained after 7 h of polymerization vs. 10–15 branches/1000 C atoms for low-density polyethylene).

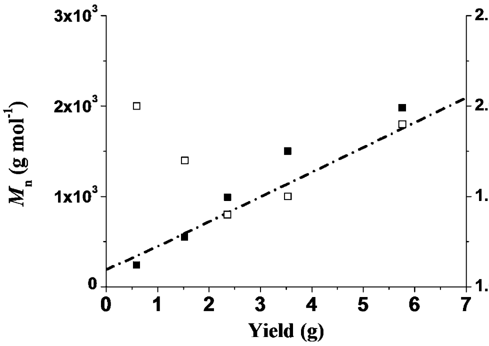


Figure 2. Evolution of number-average molar mass (experimental: ■, theoretical: –•–•) and dispersity (□) from high-temperature SEC with polymerization yield.

The quality of the control was further investigated by an in-depth study of the chemical structure of the obtained polyethylenes in the presence of **1**, with a particular emphasis on the characterization of chain ends. The ^{1}H and ^{13}C NMR spectra of polyethylenes obtained after 1, 3, and 7 h of polymerization are shown in Figures 3 and S3, respectively.

After one hour of polymerization, ^{1}H NMR analyses showed the quantitative consumption of **1**, as the singlet corresponding to the methylene group in between the sulfur atom and the ester group in **1** (see the Supporting Information, Figure S1) is no longer present. In addition to the characteristic resonances of polyethylene at 1.3 ppm (meth-

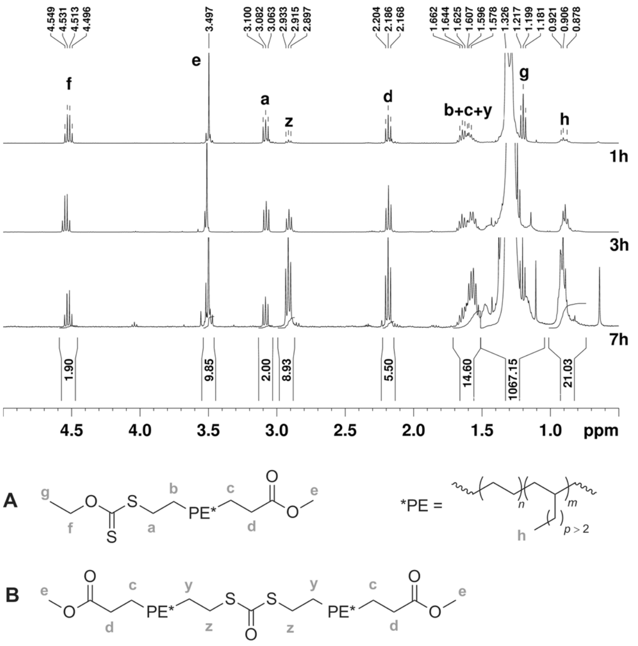
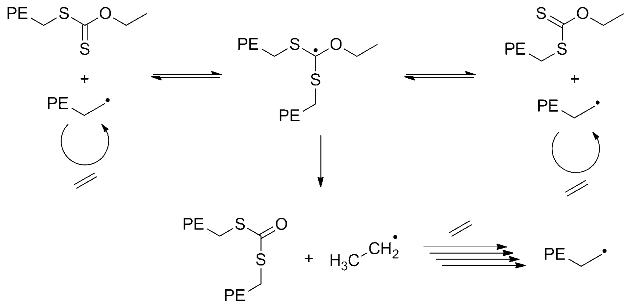


Figure 3. ^{1}H NMR spectra of polyethylenes obtained after 1, 3, and 7 h of polymerization in the presence of **1** (at 90 °C in C_6D_6/TCE 2/1 v/v). Number of branches: 2–4 branches/1000 C atoms determined by ^{13}C NMR spectroscopy (Figure S3). TCE = tetrachloroethylene.

ylene groups of the main chain), well-resolved signals can be assigned to the presence of an *O*-ethyl xanthate chain end (protons g and f) and to the reinitiating fragment of **1** (protons e and d). Resonances a, b, and c confirmed the expected polyethylene structure **A** depicted in Figure 3. An additional methylene resonance was observed at 2.9 ppm (triplet noted as z on the NMR spectra in Figure 3), the intensity of which increases with the polymerization time. The intensity of the resonances corresponding to protons a of the methylene group adjacent to the sulfur atom in **A** decreased concomitantly. These data showed the appearance with time of a new methylene group at 2.9 ppm adjacent to a sulfur atom. With the help of ^{13}C NMR analyses (Figure S3), the appearance of an additional carbonyl signal led us to consider the formation of polyethylene chains with structure **B** (Figure 3).



Scheme 2. Side fragmentation of the *O*-ethyl group in ethylene RAFT polymerization mediated by **1**.

Structure **B** could originate from the fragmentation of the *O*-ethyl bond during the RAFT polymerization of ethylene (Scheme 2). This fragmentation was reported by Barton for deoxygenation of alcohol.[21] However, this fragmentation reaction is usually not observed in RAFT polymerization.[22] Indeed, the similar stability of the growing polyethylenyl radicals and the ethyl radicals produced after this side fragmentation favors the formation of **B** in our system. In addition, once **B** is formed, further addition of growing radicals onto the C=O bond of **B** is not favored,[23] which can explain the aforementioned broadening of the molar mass.

Chain-extension experiments with ethylene were used to assess whether the obtained polyethylene chains were still living. Polyethylene–xanthate (PE-X, $M_n = 550\ \text{g mol}^{-1}$, $Đ = 1.7$, functionalization rate 80%) was employed and the reaction was carried out in DMC at 70 °C and 200 bar of ethylene pressure over 7 h. The molar ratio PE-X/AIBN was kept to 9. As shown in Figure 4, the expected shift of the peak corresponding to the final polymer was observed, although the peak broadened ($Đ = 3.4$) with respect to the chromatogram of the initial PE-X. A shoulder responsible for this broadening and corresponding to the presence of the starting material is observable in the final product. This is consistent with the side fragmentation evidenced above, leading to a fraction of chains that cannot be reinitiated. This result showed the livingness of the majority of the chains of PE-X.

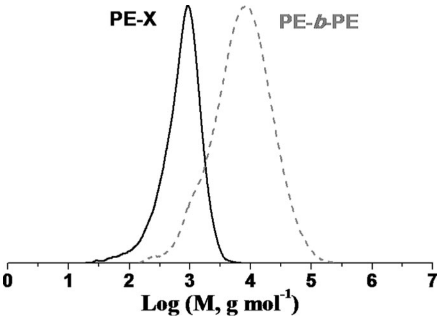


Figure 4. Evolution of molar mass distribution during the chain-extension reaction with ethylene of a polyethylene-xanthate synthesized in the presence of **1**.

We next investigated the use of vinyl acetate (VAc) as a comonomer in the RAFT polymerization of ethylene mediated by **1**. A particular focus was put on a low VAc content and semicrystalline copolymers, as they are of industrial interest[5] and their controlled synthesis has never been reported.[15] Experiments were carried out in VAc/DMC mixtures (5/95 and 25/75 v/v%) over 3, 5, and 7 h and under 200 bars of ethylene pressure (Table S1). As shown in Figures S4 and S5, a well-defined shift of the molar mass distributions was observed and the evolution of M_n as a function of the yield was linear in both cases. The dispersity values ranged between 1.5 and 2.0. These results attested the control of the copolymerization. ^{1}H NMR analyses were performed on the copolymers isolated after 5 h of polymerization (Table S1). 2 and 9 mol% of the VAc unit were incorporated in the copolymer isolated from experiments 17 (5 vol% of VAc in the starting VAc/DMC mixture) and 20 (25 vol% in the starting VAc/DMC mixture), respectively, which remain crystalline as attested by DSC measurements (melting points of 106 °C and 81 °C for copolymers from experiments 17 and 20, respectively). The NMR spectra (see the Supporting Information, Figure S6) showed the absence of the resonance of a methine proton of a VAc unit adjacent to a xanthate chain end and expected at 6.7 ppm. Thus, the exclusive presence of ethylene units adjacent to the xanthate end functionality made the side fragmentation reaction observed in the case of homopolymerization of ethylene unavoidable. This was characterized by the resonance of protons z at 2.9 ppm (Figure S6).

To side step this unwanted side fragmentation, we considered **2** as controlling agent. The presence of a methyl group as R group in **2** instead of an ethyl in **1** should hamper this side reaction during the course of the ethylene polymerization, because it will lead to less stable methyl radicals.[22] A series of experiments was thus conducted under our previous conditions in the presence of **2** (see experiments 6 to 15 in Table S1). These two systems behaved very similarly (no impact of the presence of **2** on the kinetics, same polymerization rates) and the same level of control was observed in the presence of **2** (M_n close to theoretical values and low $Đ$). A careful examination of the ^{1}H NMR spectra recorded on the final polymers obtained after different times of polymerization showed the presence of the population resulting from the side fragmentation of the methyl group (Figure S7 NMR comparison). For both series of experiments (performed in the presence of **1** or **2**), the proportions of xanthate end-functionalized chains (**A** type in Figures 3 and S7) and *S,S*-dithiocarbonate containing chains (**B** type in Figures 3 and S7) was determined using ^{1}H NMR analyses. As shown in Figure S8, the proportion of chains that underwent the side fragmentation with **2** was considerably reduced.

In conclusion, RAFT polymerization of ethylene was performed using xanthates as controlling agents. The livingness of the process was shown by the increase of the number-average molar mass versus the yield and by PE chain-extension experiments in the presence of ethylene. Semi-crystalline copolymers of ethylene and vinyl acetate were further produced under mild conditions and exhibited low contents of VAc unit ($< 10\,\%$). This work opens up an avenue for the design of powerful controlling agents for free-radical ethylene polymerization under mild conditions.

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