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Aromatic xanthates and dithiocarbamates for the polymerization of ethylene through reversible addition–fragmentation chain transfer (RAFT)

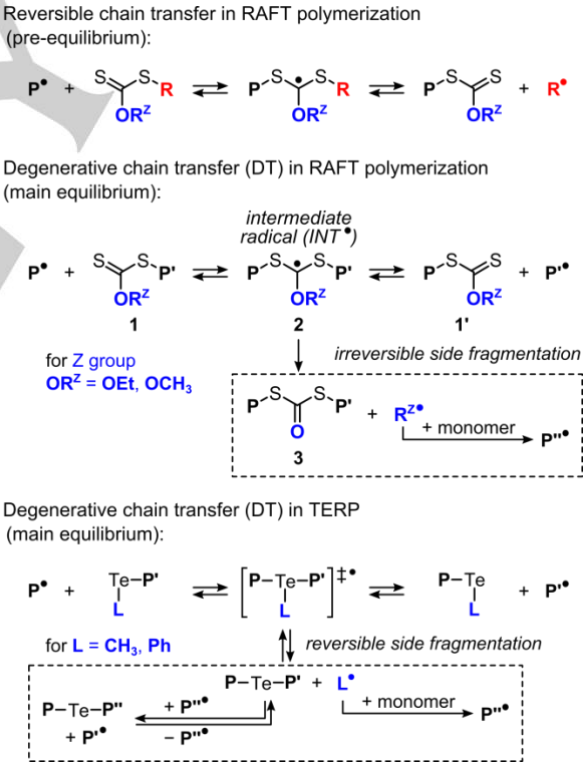
Arne Wolpers, Cédric Bergerbit, Bastian Ebeling, Franck D'Agosto,* Vincent Monteil*

Abstract: Aromatic xanthates and dithiocarbamates were used as chain-transfer agents (CTAs) in reversible addition–fragmentation chain transfer (RAFT) polymerizations of ethylene under rather mild conditions (≤ 80 °C, ≤ 200 bar). While detrimental side fragmentation of the intermediate radical leading to a loss of living chain-ends was observed in a previous study of alkyl xanthate CTAs, this mechanism was absent for the aromatic CTAs. The loss of living chain-ends was nevertheless detected for the aromatic xanthates via a different mechanism based on cross-termination. Narrow molar-mass distributions with dispersities between 1.2 and 1.3 were still obtained up to number average molar masses M_n of 1000 g mol^{-1}. In contrast, the loss of chain-ends was minor for dithiocarbamates, yielding polyethylene up to M_n = 3000 g mol^{-1} with dispersities between 1.4 and 1.8. While all systems investigated showed significant rate retardation, the dithiocarbamates are indeed the first CTAs giving polyethylene with a high livingness via RAFT polymerization, which finally offers the possibility to readily synthesize various new polyethylene-based polymer architectures.

Introduction

Reversible deactivation radical polymerization (RDRP)[1] is a mature technology that has been extensively studied for almost twenty-five years.[2,3] The vast majority of monomers polymerizable via a conventional free radical mechanism have been successfully used in RDRP, leading to a myriad of new polymer architectures and properties. However, the RDRP of some monomers, including several monomers of major industrial importance,[4–6] remains challenging. Ethylene, which leads to polyethylene (PE), the most-produced polymer worldwide, is one such monomer. Ethylene is gaseous under ambient conditions and requires specific expertise for its polymerization in autoclaves. With a critical point at 50.4 bar and 9.2 °C, ethylene becomes a supercritical fluid above these conditions. Polymerization therefore takes place in a more complex medium than for most conventional liquid monomers.[7] In addition, propagating polyethylenyl radicals (PE$^{\bullet}$) are very reactive. Generating this reactive species through homolytic bond cleavage is difficult, which rules out RDRP techniques based on reversible termination (e.g., nitroxide-mediated polymerization[8] or atom-transfer radical polymerization[9,10]). Techniques based on degenerative chain-transfer (DT), on the other hand, offer more promise for controlling ethylene polymerization.[11,12] We recently showed the first successful reversible addition–fragmentation chain transfer (RAFT) polymerization of ethylene using alkyl xanthates[13] and organotellurium-mediated radical polymerization (TERP) of ethylene[14] under rather mild (for ethylene) polymerization conditions (200 bar, 70 °C).[15,16]

Scheme 1. (a) Pre-equilibrium and main equilibrium in RAFT[13] and (b) main equilibrium in TERP[14] with the respectively observed side fragmentation for ethylene polymerizations. P, P', and P'' represent polymer chains.



Although the investigated RAFT system demonstrated controlled chain growth (with molar masses of PE increasing linearly with increasing ethylene conversion), a distinct side reaction, identified as *side fragmentation,* could be observed (see Scheme 1a).[17] In side fragmentation, the intermediate radical (INT$^{\bullet}$) **2** fragments to give radical R$^{Z\bullet}$ and polymer **3**, where polymer **3** features two chains bound by one dithiocarbonate SC(=O)S bridge. (While the same reaction can occur in the pre-

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Supporting information for this article is given via a link at the end of the document.

equilibrium, it is omitted for clarity in Scheme 1a.) This side reaction is caused by the rather low stability of the propagating PE•, promoting side fragmentation as a competitive reaction to DT and releasing a similarly unstable alkyl radical R^{Z}•. 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. This not only diminishes chain-growth control but also incessantly reduces the amount of living and end-functionalized chains. To the best of our knowledge, the described RAFT system was the first one where side fragmentation could be observed experimentally, while side fragmentation had been predicted earlier by a theoretical study of RAFT polymerizations of vinyl acetate (VAc).[18]

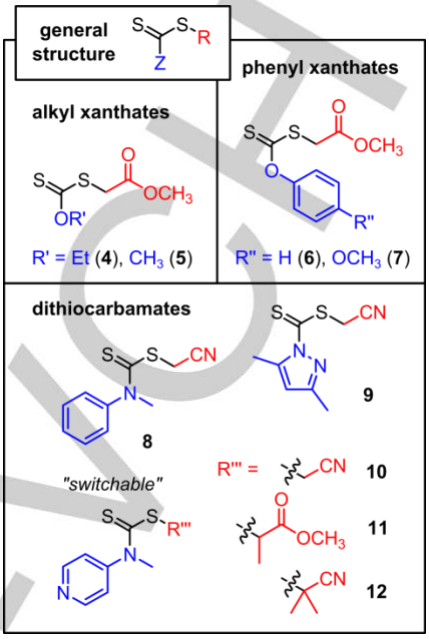
In our earlier work,[13] we showed that a chain-transfer agent (CTA) with Z = OCH_3 (**5** in Chart 1) leads to less (yet still pronounced) side fragmentation than one with Z = OEt (**4**). The •CH_3 species is less stable than Et• and its formation through side fragmentation is therefore less favoured. One study reported ethylene (co)polymerization using **5** without addressing side fragmentation.[19] In TERP of ethylene, we detected a comparable side-fragmentation mechanism that has never been observed for any other monomer type either (see Scheme 1b).[14] This reaction is reversible, so no dead chains are generated, but molar-mass control is still reduced because the formed PE–Te–PE species undergoes slower chain transfer and has roughly twice the molar mass of the PE–Te–L species of the DT (with L being the stabilizing group). The side reaction could be virtually eliminated when L was changed from CH_3 to a Ph group, since the Ph group is even less prone to fragmentation.

In the present publication, we apply this rather straightforward strategy to suppress side fragmentation in the RAFT polymerization of ethylene. We advance from the previously-studied alkyl xanthates **4** and **5** to the *aromatic* xanthates and dithiocarbamates **6–12** and investigate their potential as effective CTAs for RAFT polymerization of ethylene.

Experimental Section

The experimental setup and conditions used for the polymerization of ethylene are similar to those used in our previous studies,[13,14] and briefly described in the following. In a typical procedure, the radical initiator 2,2'-azobis(2-methylpropionitrile) (AIBN) and the CTA were stirred in 50 mL of dimethyl carbonate (DMC) in a 160 mL autoclave reactor at either 70 °C or 80 °C, and at a constant ethylene pressure between 60 bar and 200 bar. In a limited number of runs, an autoclave with a sapphire window was used in the same conditions, and it was observed that upon polymerization, the formation of insoluble PE rendered the initially clear solution turbid. After a predetermined polymerization time, the reactor was cooled down, opened, and the contents were collected with toluene. Ethylene conversion was determined gravimetrically. The polymer was analyzed via size-exclusion chromatography (SEC, in 1,2,4-trichlorobenzene at 150 °C, conventional calibration with linear PE) to determine its molar-mass distribution (MMD) and via NMR spectroscopy (in benzene-d_6/tetrachloroethene, 1:2 by volume, at 90 °C). The materials used, experimental setup, polymerization procedure, and analytical methods are described in more detail in the Supporting Information.[20–22]

Chart 1. CTAs for RAFT polymerizations of ethylene used in our earlier work[13] (**4**, **5**) and in the present one (**4**, **6–12**).



Results and Discussion

Xanthates and dithiocarbamates are known to destabilize INT•[23,24] (Scheme 1a) and are thus ideal for the polymerization of less-activated monomers (LAMs) like ethylene or VAc. Especially attractive are the so-called "switchable" agents **10–12** since post- or pre-protonation of the N atom in the pyridyl ring significantly increases the stabilization of INT• and would thus additionally allow the polymerization of more-activated monomers (MAMs) like styrene or (meth)acrylates.[25] **9** was recently reported to control the chain growth in polymerizations of VAc and was thus evaluated as well.[26]

Polymerizations with *O*-aromatic xanthates

Polymerizations were conducted at 70 °C and 200 bar of ethylene using 50 mg of AIBN (6.09 mmol L^{-1}) and the xanthate CTAs **4**, **6**, or **7** (18.3 mmol L^{-1}, with a concentration ratio [CTA]:[AIBN] of 3:1). We decreased the concentration of CTA compared to our previous work on **4** and **5**, in which we used [CTA]:[AIBN] = 10:1 and 50 mg of AIBN.[13] All aromatic xanthates (**6**, **7**) and dithiocarbamates (**8–12**) resulted in retardation, and acceptable polymerization rates could only be attained by reducing their concentrations. Figure 1a shows the ethylene conversion versus polymerization time for the respective xanthate systems in comparison to a conventional polymerization system with no CTA.

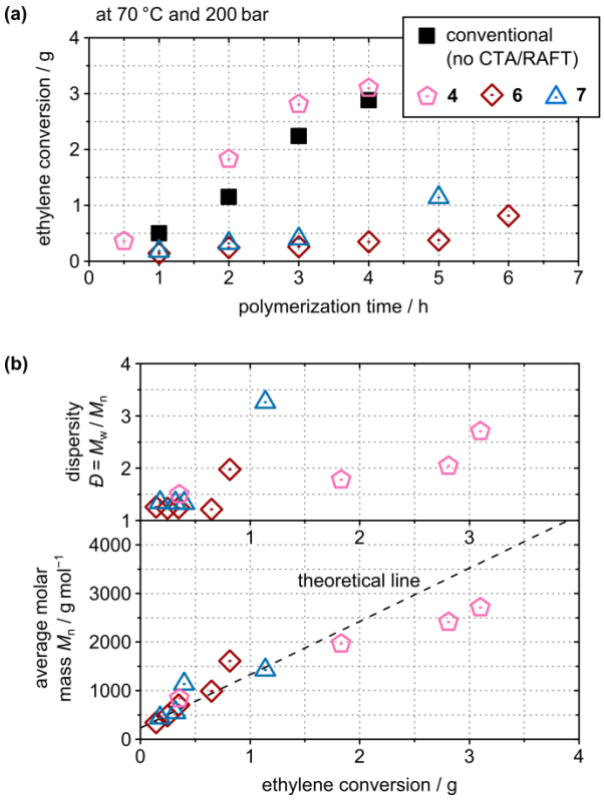


Figure 1. (a) Ethylene conversion versus polymerization time for RAFT systems with xanthates **4**, **6**, and **7** in comparison to the conventional radical polymerization system without a CTA and (b) the corresponding molar-mass evolutions. The conventional radical polymerization system yielded PE with M_n values between 8000 and 13 000 g mol^{-1} and $Đ$ values between 2.0 and 3.7.

Consistent with our earlier work, the use of the *alkyl* xanthate **4** did not lead to retardation compared to the conventional system. It even slightly increases the polymerization rate, a behavior rather atypical for RAFT systems. This might stem from a small impact of **4** on the polarity of the medium, as we have already shown that the yield of PE strongly depends on the polarity of the solvent used in the polymerization.[15] In contrast to **4**, the *aromatic* xanthates **6** and **7** drastically decrease the polymerization rate to an extent that appears to be too great to be caused by polarity effects alone. Retardation might be caused by the expected strong stabilization of INT$^{\bullet}$ in the RAFT equilibrium by the aromatic Z-groups, reducing the amount of PE$^{\bullet}$.[20] In addition, retardation might be a result of the impact of the respective Z-groups on the reduction of side fragmentation,[22] which will be explained below.

As in our earlier work, the system with **4** showed very pronounced side fragmentation and formation of species **3**. Figure 2a shows a ^{1}H NMR spectrum of PE obtained with **4** after 2 h of polymerization. The formation of the side-fragmentation product can be quantified by the signal of the protons h neighboring the SC(=O)S unit in relation to the protons c neighboring the living xanthate unit. 33% of the living chains were transformed into species **3** after 1.9 g of ethylene conversion (2 h of polymerization time), 56% after 2.9 g (3 h), and 65% after 3.1 g (4 h). Another ^{1}H NMR spectrum of PE obtained with **7** after 5 h of polymerization is shown in Figure 2b. While the Z-group of **7** is different from **4,** and thus the shift of the signal of the protons m slightly differs from c (cf. Figure 2a), the shifts of the signals of the protons from the identical (re)initiating group do not change (o/p/q = e/f/g). Upon side fragmentation, PE derived from both **4** and **7**—and any other xanthate for that matter—loses its distinguishing R^Z-group, leading to the same product of two chains being connected by one SC(=O)S bridge. However, in the spectrum in Figure 2b, no signal of the characteristic proton h is observed. This observation applies to all PEs synthesized with either **6** or **7** in the entire publication, indicating that indeed no significant side fragmentation takes places in case of a phenylic leaving group.

While a pronounced stabilization of INT$^{\bullet}$ by the Z-groups of **6** and **7** can cause retardation, the lack of side fragmentation might be another crucial reason for the rather low polymerization rates. As a general characteristic of RAFT polymerization, INT$^{\bullet}$ is usually not active enough to (re)initiate a significant amount of new chains. For systems with **4** or **5**, side fragmentation, along with the normal fragmentation in the RAFT equilibrium, generates a radical that can effectively (re)initiate polymerization. However, the side fragmentation mechanism does not exist for either **6** or **7**. The average lifetime of INT$^{\bullet}$ is thus expected to be longer, which could slow down polymerization. A longer lifetime of INT$^{\bullet}$ might also explain another feature observed in the systems with **6** or **7**: the systematic increase of signals in the ^{1}H NMR spectrum between 2.3 ppm and 2.8 ppm, as well as in the aromatic region, accompanied by the decrease of all signals stemming from protons close to the CS_2 end-group (j–n for **7** in Figure 2b). This indicates that the CS_2 end-group is indeed consumed and chain-end functionality is lost, even if it does not happen through side fragmentation. The extent of loss of chain-end functionality over ethylene conversion increases similarly to that observed for **4**, with 32% after 0.8 g of ethylene conversion for **6** (after 6 h of polymerization) and 23% after 1.1 g for **7** (after 5 h), which was determined from the CH_2 protons neighboring the CS_2 unit and the R-group (cf. m and p in Figure 2b). While the exact reaction mechanisms are still unclear, the observed NMR signals might partly stem from reaction products following cross-termination between PE$^{\bullet}$ and INT$^{\bullet}$. This reaction is expected to be particularly pronounced for rather long lifetimes and thus higher concentrations of INT$^{\bullet}$. As our reasoning on this matter is somewhat lengthy and should not become the main point of this publication, it is more thoroughly described in the Supporting Information.[27–34]

Figure 1b shows the dispersity, $Đ$, and average molar-mass values, M_n, from the polymerization systems discussed so far. While the conventional system gave high and constant M_n values early in the process (between 8000 and 13 000 g mol^{-1} with $Đ$ from 2.0 to 3.7, data not shown), all M_n values of the RAFT systems increase linearly with increasing ethylene conversion, which is theoretically expected in an RDRP.

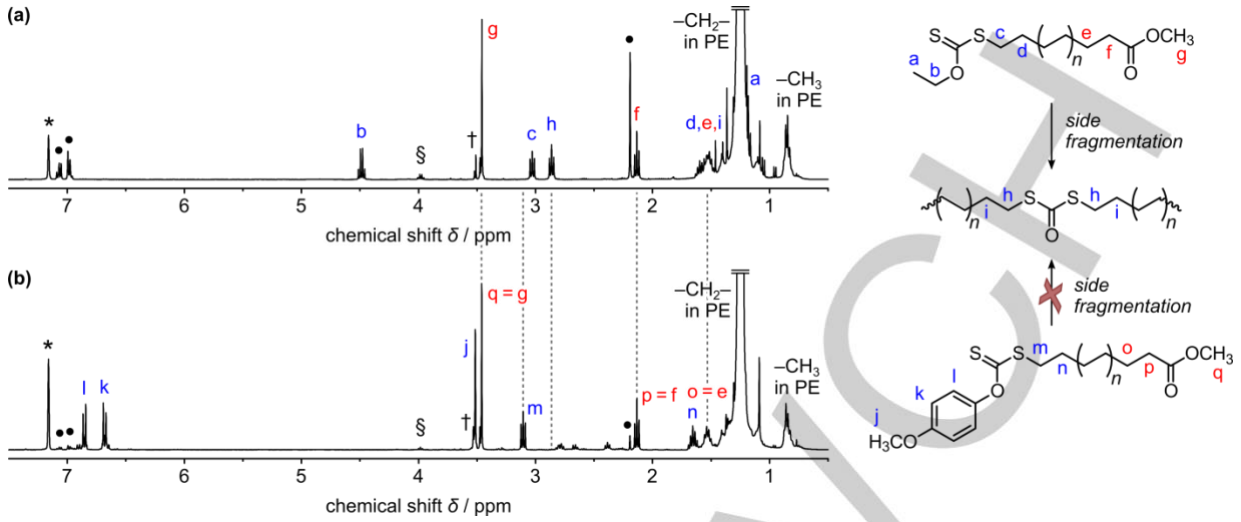


Figure 2. ^{1}H NMR spectra of PE synthesized in the presence of (a) **4** (cf. Figure 1, after 2 h) and of (b) **7** (after 5 h). The end group –CH_3 stems either from intramolecular chain transfer inherent in ethylene radical polymerization or from (re)initiation of polymerization in case of side fragmentation for **4**. *NMR solvent benzene, †polymerization solvent DMC, §transfer to DMC, ˙collecting solvent toluene.

The MMDs of PE from **4** are unimodal and broaden from *Đ* of about 1.5 to 2.2, reaching $M_n \approx 3000$ g mol^{-1}. For **6** and **7**, the MMDs are remarkably narrow at the beginning of the polymerization with *Đ* values as low as 1.2 for $M_n \leq 1000$ g mol^{-1}, indicating the beneficial impact of the aromatic Z-groups on chain-growth control. For $M_n > 1000$ g mol^{-1}, however, the MMDs broaden due to the evolution of a peak at high molar masses, which leads to a drastic increase of *Đ*. Figure 3 shows the MMDs for **6** from 1 h to 6 h (similar MMDs could be observed for **7**). While they are narrow and shifting to higher molar masses, the appearance of a second distribution can be seen after 6 h. It is likely that this high-molar-mass peak originates from a conventional radical polymerization of ethylene, which will be explained below.

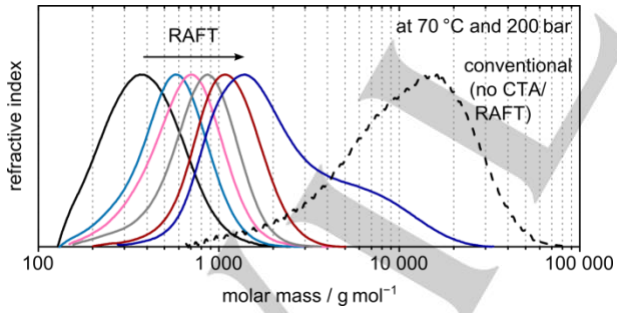


Figure 3. MMDs of PE produced in a conventional system (no CTA/RAFT) after 1 h and in the presence of **6** after 1, 2, 3, 4, 5, and 6 h. At 6 h, the appearance of a high molar-mass species can be observed.

In order to increase the polymer yield, polymerizations were also conducted at 80 °C instead of 70 °C under otherwise identical conditions. The ethylene conversion versus time and the molar-mass evolution of polymerizations with **6** and **7** are presented in Figure 4 (series “80 °C, 200 bar”).

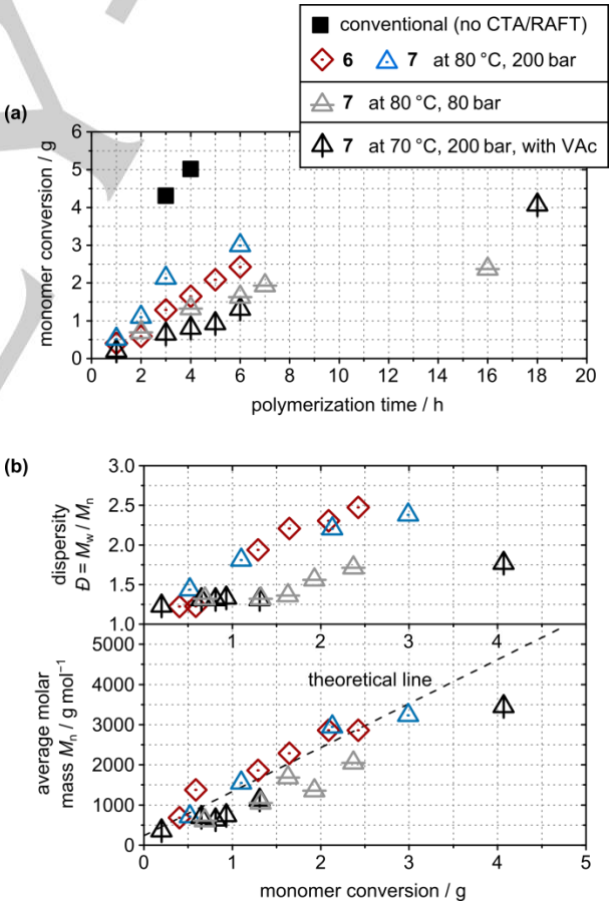


Figure 4. (a) Monomer conversion versus polymerization time for RAFT systems with xanthates **6** and **7** in comparison to the conventional radical polymerization system without a CTA and (b) corresponding molar-mass evolutions. Polymerization temperature and ethylene pressure as indicated. For polymerizations without VAc: monomer conversion = ethylene conversion, for polymerizations with VAc: monomer conversion = conversion of both ethylene and VAc.

All effects described for 70 °C were also observed for 80 °C, while the most significant difference was simply the expected higher PE yields. As for 70 °C, systems with **6** and **7** exhibit low *Đ* values at the beginning of the polymerization that increase after M_n = 1000 g mol^{-1} due to the evolution of a high-molar-mass species—the MMDs for **6** are shown in Figure S1.

The high-molar-mass peak arguably stems from a conventional polymerization, i.e., a polymerization without significant participation of RAFT. The peak closely matches the MMD obtained from the CTA-free conventional polymerization of ethylene (see Figure 3). As PE yields increase, this peak stays at similar molar masses and only increases in intensity, while the RAFT peak ceases to shift toward higher molar masses (Figure S1). Furthermore, while the polymerization is very slow for **6** and **7** at 70 °C, the polymerization rate increases after the first appearance of the high-molar-mass species (last respective data point of both series in Figure 1a), supporting a non-RAFT mechanism.

The reason the RAFT mechanism is no longer significant could lie in the dispersion behavior of the polymer. In experiments that were carried out in a reactor with a sapphire window, we could see that for 50 mL of pure DMC as the solvent, the system remained phase-separated (bottom phase: DMC with dissolved ethylene; top phase: supercritical ethylene) up to ethylene pressures of about 95 bar. At higher pressures, the system turned into a single supercritical DMC/ethylene phase, as expected from thermodynamic calculations.[7] When polymerizations with **7** were carried out at pressures lower than 95 bar, namely at 80 bar (see Figure 4, series "80 °C, 80 bar" compared to series "80 °C, 200 bar"), MMDs stayed unimodal during the polymerization up to molar masses of about 2000 g mol^{-1}, far from the MMD of the respective conventional polymerization system (see Figure 5). The two-phase system at lower pressure (80 °C, 80 bar) thus showed better control than the comparable supercritical system (80 °C, 200 bar). To further explore the connection between the state of the system employing **7** and its chain-growth control, we increased the pressure of a polymerization from originally 80 bar (two phases) to 120 bar (supercritical) within a few seconds.

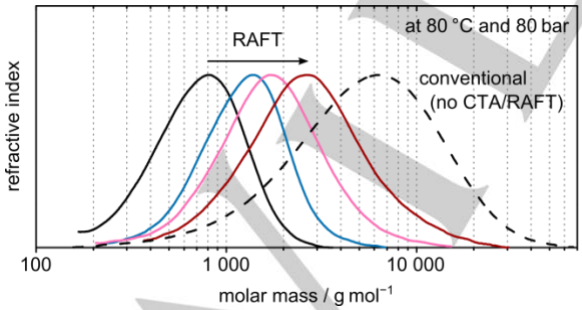


Figure 5. MMDs of PE produced in a conventional system (no CTA/RAFT) after 4 h and in the presence of **7** after 2, 4, 7, and 16 h.

The originally well-dispersed suspension of PE particles broke down and the particles agglomerated and stuck to the walls of the reactor. We believe that this effect might be related to a poorer dispersion of PE with the phenoxy-type Z-end-groups from either **6** or **7** in supercritical DMC/ethylene compared to non-supercritical DMC. If this dispersion state prevents the solvent from effectively accessing and swelling PE in the region of the living chain-ends, they will no longer participate in the reaction phase. As a result, for the rest of the polymerization, PE is no longer produced via a RAFT mechanism but only via a conventional radical polymerization mechanism. During this conventional polymerization, dead PE is generated while the PE chains that feature a RAFT end-group simply remain in the system without further participation in the polymerization. Indeed, ^{1}H NMR still shows RAFT-group-functionalized PE even after chain-growth control has already ceased (cf. Figure 2b, signal m, with about 77% of chains that are still living). Polymerizations at pressures that are only slightly higher than 95 bar, namely 100 or 120 bar, already show the presence of a high-molar-mass species for M_n > 1000 g mol^{-1} (Figure S2). It should be stated that for polymerizations at 80 bar, the same chain-end transformation was observed as for 200 bar (cf. Figure 2b, signals between 2.3 and 2.8 ppm as well as in the aromatic region). This clarifies that the two observed effects of losing chain-end functionality and the occurrence of a conventional radical polymerization do not go hand in hand.

Copolymerizations of ethylene with VAc using aromatic xanthates were also investigated to see whether well-defined poly(ethylene-*co*-vinyl acetate) (EVA) could be obtained in the absence of the side-fragmentation product.[13] In addition, these systems provide more information on the effect of dispersion/solubility on the formation of high-molar-mass chains. CTA **7** was employed at 70 °C and 200 bar of ethylene pressure. Instead of 50 mL of DMC, 38 mL of DMC together with 12 mL of VAc (total volume of 50 mL) were used, while all other conditions remained unchanged. The polymerization results in Figure 4 (series "70 °C, 200 bar, with VAc") show good chain-growth control, while the MMDs stay unimodal throughout the whole polymerization process (Figure S3), with no high-molar-mass chains arising from conventional radical polymerization. The EVA product (^{1}H NMR analysis showed VAc contents of 10 mol%) is more soluble in DMC than is PE (e.g., at 80 °C, the EVA was found to be completely soluble in DMC, whereas PE was completely soluble only for molar masses lower than 500 g mol^{-1} and completely insoluble for molar masses higher than 2000 g mol^{-1}). The EVA is thus also expected to be much more soluble in the supercritical DMC/ethylene mixture than PE. As observed in our earlier work,[13] ^{1}H NMR spectra showed no VAc units next to the CS_2 group (i.e., no characteristic signal at about 6.7 ppm), leaving all chains with an ethylene ultimate unit. Since the CTA-bearing chain-ends were identical to those in the PE systems, loss of end-groups could also occur as for pure PE using **7**. The fact that end-group loss occurred without the formation of high molar mass chains highlights that the two phenomena are not related.

Polymerizations with *N*-aromatic dithiocarbamates

Polymerizations of ethylene were also conducted with dithiocarbamates **8–12** at 70 °C and 80 °C under the same conditions cited above. Systems with **9** showed a very strong retardation. This behavior is expected as INT$^\bullet$ with Z =

dimethylpyrazolyl shows by far the lowest tendency to undergo fragmentation of all the CTAs used in the present work.[26,35] As a result, systems with **9** produced PE only for rather low CTA and high AIBN concentrations ([CTA]:[AIBN] = 0.5:1 and 100 mg of AIBN compared to the normal conditions of [CTA]:[AIBN] = 3:1 and 50 mg of AIBN). Molar mass and NMR data indicated no participation of **9** in an RDRP process under these conditions and it will therefore not be further discussed. The polymerization results of the other dithiocarbamates at 70 °C and 200 bar are shown in Figure 6. As for the aromatic xanthates, a pronounced retardation is obtained for all systems. The polymerization rates decrease in the following order: **8** > **11** > **10** ≈ **12**.

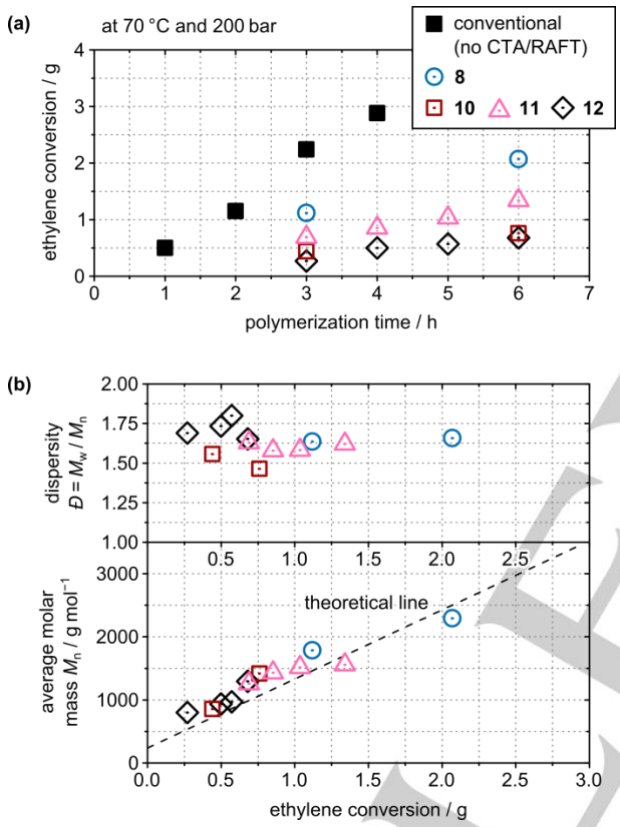
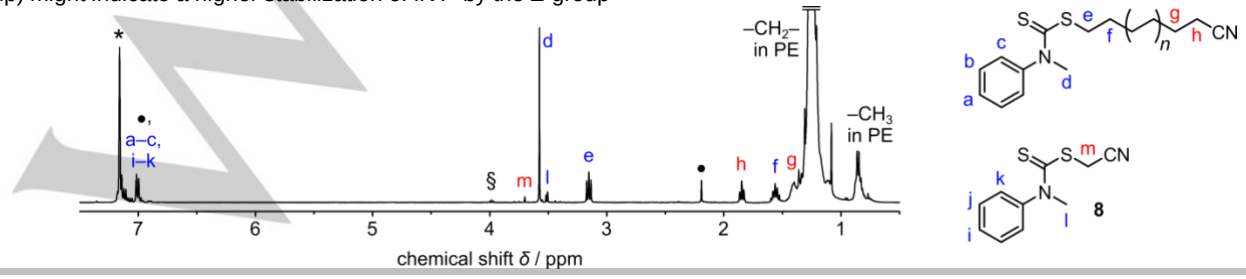


Figure 6. (a) Ethylene conversion versus polymerization time for RAFT systems with dithiocarbamates **8**, **10**, **11**, and **12** in comparison to the conventional radical polymerization system without a CTA and (b) corresponding molar-mass evolutions. The conventional radical polymerization system yielded PE with M_n values between 8000 and 13 000 g mol^{-1} and $Đ$ values between 2.0 and 3.7.

The difference between **8** and **10** (identical R-group, different Z-group) might indicate a higher stabilization of INT• by the Z-group of **10** and/or a higher reactivity of **10** with PE• compared to **8**. The trend of **11** > **10** ≈ **12** (identical Z-group, different R-group) might stem from different abilities of the released radical R• to (re)initiate another PE chain. All systems show very good agreement with the theoretically expected M_n values, while the obtained $Đ$ values are rather constant between 1.4 and 1.8. In contrast to the aromatic xanthate systems, MMDs stay unimodal throughout the entire polymerizations up to M_n much greater than 1000 g mol^{-1}, suggesting that the described dispersion effect is less significant for dithiocarbamates. Examples of the MMD of PE from **11** are presented in Figure S7. More importantly, the loss of chain-ends is minor for both **8** and **10**. As was the case with the aromatic xanthates, no sign of side fragmentation was present. However, in contrast to the xanthates, the ^{1}H NMR signals between 2.3 ppm and 2.8 ppm were very weak to the point of being difficult to detect for PE produced from **8** or **10**. The intensity ratio between the signals of the protons neighboring the CS_2 unit and those neighboring the CN of the R-group stayed constant and close to unity during all polymerizations, indicating no significant loss of chain-end functionality. Figure 7 shows an example of a spectrum of PE from **8** (after 6 h of polymerization) with the corresponding respective signals d/e and h. In contrast to **8** and **10**, the quantification of chain-end functionality is not possible for either **11** or **12** as the signals of the protons at the respective R-groups are superimposed by either the –CH_2– or the –CH_3 units of PE. Nevertheless, the chain-end functionality of PE from either **11** or **12** is expected to be similar to the one of PE from **10**, because a potential chain-end degradation would happen at the CS_2 end-group, which is identical for **10**, **11**, and **12**. Still, the decomposition signals between 2.3 ppm and 2.8 ppm are slightly more intense in the case of **11** and **12** compared to **10**, so that an impact of the R-group cannot be ruled out at the moment. The systems with **8** and **10** are indeed the first RAFT polymerizations of ethylene that do not suffer from a loss of chain-ends and thus show high chain-end functionality. Looking at the Z-groups of the dithiocarbamates, one might intuitively reason that side fragmentation could happen through the release of the •CH_3 radical just as for **5**. However, since this is not observed, the formation of the corresponding dead polymer bearing a C=N double bond or the formation of following products is arguably not very favorable.

Polymerizations at 80 °C (see Figure 8) led to higher ethylene conversion, and thus M_n, and all trends already described for 70 °C were observed. Values of M_n lower than the theoretical values can be observed for higher ethylene conversion obtained with **8**. This phenomenon was also observed in our earlier works and was attributed to the inevitable irreversible termination of PE• as well as continuous initiation of new chains by AIBN.[14] All investigated dithiocarbamates are solid at room temperature and therefore remain in the polymeric product after the evaporation of



the solvent when not fully consumed during the polymerization. This conveniently allowed us to quantify how quickly a given CTA is consumed in the pre-equilibrium (Scheme 1a).

Figure 7. ^{1}H NMR spectrum of PE synthesized in the presence of **8** (cf. Figure 7, after 6 h) and remaining **8**. The end group –CH_3 stems from intramolecular chain transfer inherent in ethylene radical polymerization. *NMR solvent benzene, §transfer to the polymerization solvent DMC, ˙collecting solvent toluene.

In Figure 7 for example, integration of the signals d, e, and h results in about 92% of consumed CTA **8** when compared to the signals l and m. Of all the investigated dithiocarbamates in the present work, **8** shows the slowest consumption with about 71% after a PE yield of 1.1 g and 92% after 2.1 g at 70 °C.

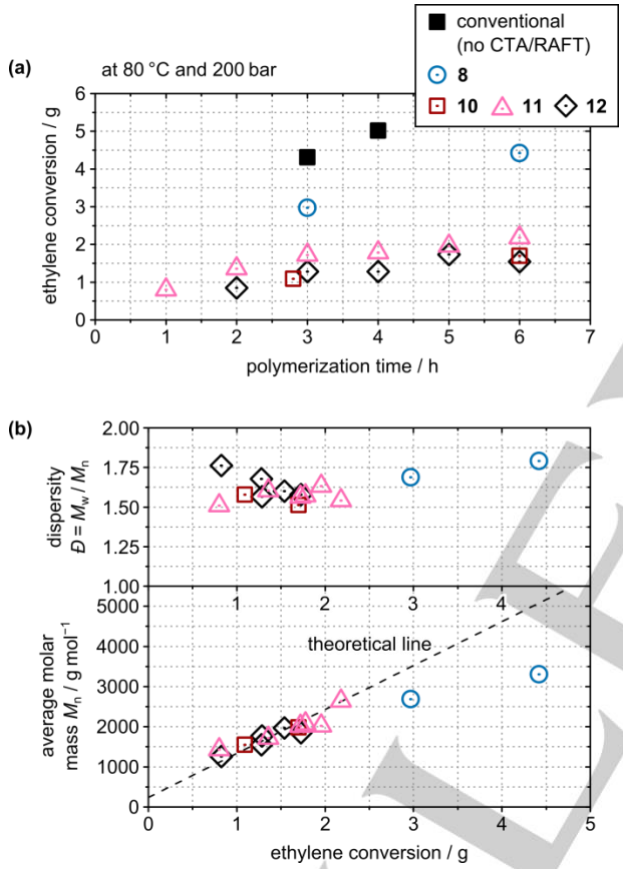


Figure 8. (a) Ethylene conversion versus polymerization time for RAFT systems with dithiocarbamates **8**, **10**, **11**, and **12** in comparison to the conventional radical polymerization system without a CTA and (b) corresponding molar-mass evolutions.

8 is consumed about three times more slowly than **10**, which shows about 74% after 0.4 g and 92% after 0.8 g. As **8** and **10** have the same R-group, this indicates that the pyridyl moiety of the Z-group significantly increases the reactivity of the CTA toward PE˙ compared with a phenyl moiety. As a result, faster addition of PE˙ is also expected during the DT main equilibrium and might lead to a generally better chain-growth control with the pyridyl moiety. By far the fastest consumption of all dithiocarbamates is that of **12,** with about 95% after 0.3 g and 97% after 0.5 g at 70 °C. This is explained by the tertiary R-group of **12** being more readily released than the primary one of **10** after the addition of PE˙ in the pre-equilibrium. It should be noted that all dithiocarbamates bearing a pyridyl moiety show more or less the same quality in terms of chain-growth control. This is reasonable, as the control of the polymerization basically depends on the frequency of the DT between two PE chains, as long as the CTA has an R-group that is at least equally likely to be released as PE˙. This is the case for all of the dithiocarbamates used in the current study.

Conclusion

By employing dithiocarbamate CTAs, we have achieved the first RAFT polymerizations of ethylene that do not suffer from a significant loss of chain-end functionality. The use of aromatic Z-groups suppressed the previously observed side-fragmentation reaction for both xanthate- and dithiocarbamate-controlled ethylene polymerizations. Unprecedentedly low *Đ* values (down to 1.2) are still obtained for the aromatic xanthates, underlining what is in principle the high activation–deactivation frequency of PE. Loss of chain-end functionality was nevertheless observed for the aromatic xanthates through a different mechanism which is not yet entirely resolved; the possible contribution of cross-termination presents another interesting avenue to explore in the world of RAFT polymerization. The detrimental impact of a supercritical DMC/ethylene phase for polymerizations performed at 200 bars with aromatic xanthates could be circumvented by using ethylene pressures lower than 90 bars.

The presented data help to make a good choice of both polymerization conditions and which CTAs to use when producing (block) copolymers based on ethylene.[36] The results also allow theoretical calculations to compare the substituent effect on the thermodynamics of the radical intermediate and the kinetics of fragmentation. Both topics are already being explored in our laboratory and will be the focus of forthcoming papers.

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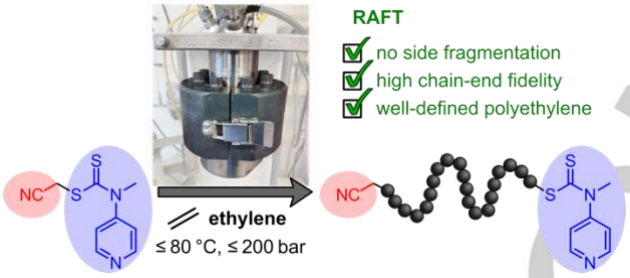
Keywords: polymerization • radicals • ethylene • reversible addition-fragmentation chain transfer (RAFT) • aryl xanthates • dithiocarbamates

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Controlled radical polymerization of ethylene was conducted through RAFT using aryl-dithiocarbonates or aryl-dithiocarbamates as controlling agents. The use of dithiocarbamates led to well-defined polyethylene chains in absence of detectable side reactions.



A. Wolpers, C. Bergerbit, B. Ebeling, F. D'Agosto, V. Monteil**

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Aromatic xanthates and dithiocarbamates for the polymerization of ethylene through reversible addition–fragmentation chain transfer (RAFT)

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