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Ethylene polymerization-induced self-assembly (PISA) of poly(ethylene oxide)-*block*-polyethylene copolymers via RAFT

Cédric Bergerbit, Florian Baffie, Arne Wolpers, Pierre-Yves Dugas, Olivier Boyron, Manel Taam, Muriel Lansalot,* Vincent Monteil,* Franck D'Agosto*

Abstract: Poly(ethylene oxide) (PEO) with dithiocarbamate chain ends (PEO-SC(=S)-N(CH₃)Ph and PEO-SC(=S)-NPh₂, named **PEO-1** and **PEO-2**, respectively) were used as macromolecular chain transfer agents (macro-CTA) to mediate the reversible addition-fragmentation chain transfer (RAFT) polymerization of ethylene in dimethyl carbonate (DMC) under relatively mild conditions (80 °C, 80 bar). While only a slow consumption of **PEO-1** was observed, the rapid consumption of **PEO-2** led to a clean chain extension and the formation of a polyethylene (PE) segment. Upon polymerization, the resulting block copolymers PEO-*b*-PE self-assembled into nanometric objects according to a polymerization-induced self-assembly (PISA).

Ethylene is the simplest and the cheapest vinyl monomer on the market. As one of the most produced and most important synthetic polymer materials, polyethylene (PE) is obtained industrially by coordination-insertion catalytic polymerization^[1-4] or by free radical polymerization (FRP) of ethylene.^[5] In addition to the economic advantages of using ethylene, PE owes its industrial success to its outstanding mechanical and thermal properties. These properties are related to the fact that PE can crystallize, enabling the polymer to be used in a vast range of applications, from packaging to joint replacement. However, PE is completely apolar and therefore a number of applications, requiring for instance surface/interface properties such as compatibility with other more polar materials (e.g. adhesion, printability) cannot be attained.^[6] A potential solution to these drawbacks is the introduction of polar moieties into the PE chains. Among the different macromolecular structures that can be targeted, polar-apolar block copolymers containing PE segments are very attractive ones. To obtain these architectures, preformed functionalized PE chains can be employed either to initiate the polymerization of a polar monomer or for coupling reactions with preformed polar segments.^[6] However, these strategies are often tedious and require multistep chemistries. Besides, the use of a living or controlled polymerization technique to directly produce block copolymers containing PE segments is often problematic. While options are available to produce living PE chains by catalytic polymerization such as living coordination-insertion^[7-9] or

coordinative chain transfer polymerization,^[10-14] the switch to a polar block faces many challenges due to the lack of compatibility of the active species with polar monomers. During the last three decades, reversible-deactivation radical polymerization (RDRP)^[15] techniques have emerged as the preferred tools for the synthesis of block copolymers. In particular, reversible addition-fragmentation chain transfer (RAFT) polymerization, using thiocarbonylthio compounds (RSC(=S)Z) as chain transfer agents (CTAs),^[16] is now established as one of the most mature and versatile methods for the RDRP of vinyl monomers. This also includes the less activated monomers, such as e.g. vinyl acetate,^[17-18] *N*-vinylpyrrolidone,^[19-21] vinyl chloride^[22] and vinylidene fluoride.^[23-24]

The range of accessible block copolymers has recently been considerably extended by the use of polymerization-induced self-assembly (PISA).^[25-28] PISA makes the most of polymerizations in dispersed media, by chain extending a solvophilic polymer that is generally^[29] but not exclusively^[30-34] produced by RAFT. The chain extension is conducted with a solvophobic block, which causes a self-assembly of the resulting block copolymers during their growth. This is made possible by the choice of a dispersing phase that is a selective solvent of the first block. As a result, PISA is not only an extremely valuable tool to efficiently produce block copolymers, including amphiphilic ones, but has also rapidly gained interest as a technique of choice to form nano-objects with various morphologies.^[29, 35-37]

Recently we have shown for the first time that RAFT polymerization of ethylene (the least activated vinylic monomer) mediated by alkyl xanthate is possible at 200 bar and 70 °C using dimethyl carbonate (DMC) as solvent.^[38] We have further shown that when aromatic dithiocarbamates were used as CTAs, PE with unprecedented chain end fidelity (*i.e.* high livingness) were obtained.^[39] Variations of the Z-group were studied to retain good control over ethylene polymerization, while the choice of the R-group was more flexible (primary (R = CH₂CN), secondary (R = CH(CH₃)COOMe) or tertiary (R = C(CH₃)₂CN) radicals had only limited impact on rate retardation). Although DMC is not a good solvent for PE, it was chosen because it is known to activate ethylene radical polymerization while minimizing undesirable chain transfer reactions.^[40] Indeed, we observed that in RAFT polymerizations of ethylene under our conditions, the formation of insoluble PE turned the initially clear solution turbid, however without affecting the control of the polymerization.^[38-39, 41]

These discoveries open up many opportunities for the design of macromolecular architectures based on PE segments including block copolymers, by means of RDRPs like RAFT. They do, however, not allow the design of the targeted polar/apolar block copolymers straightforwardly. Indeed, the resulting

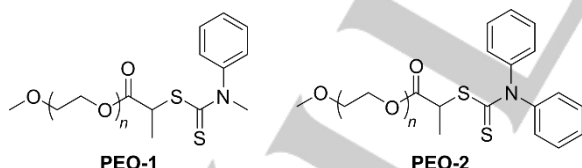
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Supporting information for this article is given via a link at the end of the document.

dithiocarbamate end functionalized PE would not lead to chain extension after a further addition of a polar monomer considering the expected blocking efficiency.^[42] Nevertheless, the gained expertise drove us to investigate the chain extension of polar segments equipped with appropriate dithiocarbamate chain ends in the presence of ethylene.^[43] We took advantage of the above-mentioned flexibility on the choice of the R group and equipped PEO chains with dithiocarbamate ends to further use them as CTA in chain extension experiments with ethylene. By performing the polymerization in DMC, the expected PEO-*b*-PE block copolymers would feature a soluble PEO segment while the growing PE segment would be insoluble, and we anticipated that a simultaneous self-assembly could occur *via* a PISA process. This paper is thus the first to report the chain extension of a preformed functionalized PEO block with PE. This is also the first time that an ethylene-PISA system is investigated.

Two PEO macro-CTAs were thus synthesized (**PEO-1** and **PEO-2**, Scheme 1), bearing a dithiocarbamate chain end with $Z = \text{N}(\text{Ph})\text{Me}$ and $Z = \text{NPh}_2$, respectively. Their syntheses are depicted in the supporting information (SI). Before performing any polymerization experiment, we visually checked that both PEO macro-CTAs were fully soluble in DMC. To confirm this qualitative assumption, dynamic light scattering (DLS) measurements were performed from two solutions of **PEO-1** and **PEO-2** in DMC at the concentrations employed in the subsequent ethylene polymerizations. At both 25 and 80 °C (the polymerization temperature), even when using the minimum attenuation, the very low value of the count rate showed that both PEO are fully dissolved in DMC and are not forming nanodomains before any polymerization takes place.

These macro-CTAs were used to mediate ethylene polymerization in DMC at 80 bar and 80 °C using azobisisobutyronitrile (AIBN) as initiator with a [macro-CTA]:[AIBN] ratio fixed to 3:1.^[39] In comparison with the FRP of ethylene performed under the same conditions, a polymerization rate reduction is observed with both macro-CTAs (Figure S1). This was assigned to a stabilization of the intermediate radicals involved in the RAFT process as already explained in our previous works.^[38-39, 41]



Scheme 1. Chemical structures of **PEO-1** and **PEO-2** dithiocarbamates.

High temperature-size exclusion chromatography (HT-SEC) analyses performed in 1,2,4-trichlorobenzene at 150 °C show a shift of the molar mass distribution (MMD) towards higher molar mass values with time, confirming chain extension (Figure 1). When **PEO-1** (Figure 1a) is used, a shoulder is systematically detected in the product formed at an elution time of 22.8 minutes, which is assigned to the starting **PEO-1** macro-CTA. The shoulder is still detected even after 6 hours of polymerization, indicating a slow consumption of **PEO-1**. On the other hand, when **PEO-2** is

used, the chain extension proceeds smoothly with a clean shift of MMDs towards higher molar mass values (Figure 1b). No shoulder is detected, indicating a fast and quantitative consumption of **PEO-2**. The MMDs become undoubtedly narrower as the polymerization proceeds, which is a characteristic of a good control of the polymerization and the formation of the targeted PEO-*b*-PE block copolymers.

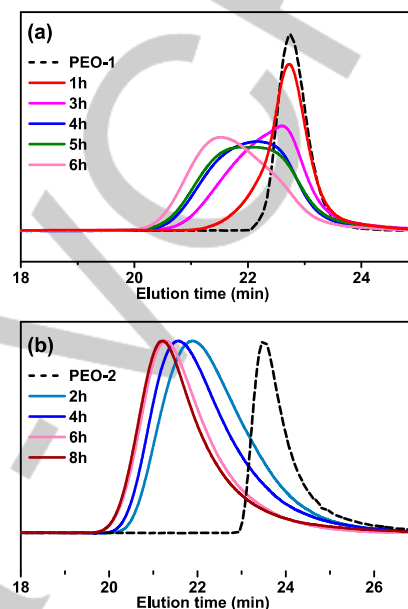


Figure 1. HT-SEC traces of the polymers resulting from ethylene polymerization in the presence of **PEO-1** (a) and **PEO-2** (b) at 80 °C and 80 bar.

Although HT-SEC has demonstrated the MMD shift of the PEO-*b*-PE formed with the polymerization time (and the PE yield), this technique does not allow an accurate determination of the molar mass values, which is due to the particular nature of the copolymer with its two blocks of fundamentally different solubility properties. ¹H-NMR analysis (performed at 90 °C in a mixture of D₆-benzene/tetrachloroethene 1:2 by volume) was thus additionally performed to (i) confirm the quantitative consumption of **PEO-2**, (ii) identify potential characteristic resonances of the targeted PEO-*b*-PE block copolymers, and (iii) determine the average molar mass value of the PE block ($M_{n,PE}$). These results are available in Table S1 in SI. As shown in Figure 2, comparison of the ¹H-NMR spectrum of the starting **PEO-2** with that of the product obtained after 4 hours of polymerization, reveals the complete consumption of **PEO-2** (disappearance of the quadruplet resonance c at 4.75 ppm). In contrast, only 86% of **PEO-1** has been converted to the desired PEO-*b*-PE after the same polymerization time (determined using the sextuplet resonance c' of the counterpart protons in PEO-C(O)CH(CH₃)-PE-SC(S)Z at 2.33 ppm, Table S1 and Figure S2).

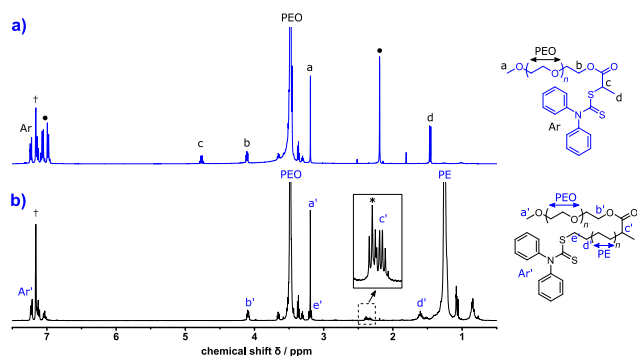


Figure 2. $^1\text{H-NMR}$ spectra of **PEO-2** (a) and after 4 hours of block copolymerization with ethylene (b), corresponding to entry 11 of Table S1. (†) NMR residual solvent benzene, (●) toluene collecting solvent.

In addition, Figure 2 supports the appearance of the characteristic triplet e' resulting from a $-\text{CH}_2-$ adjacent to the dithiocarbamate moiety seen at 3.19 ppm. This triplet is superimposed on the singlet a' corresponding to the methoxy protons of PEO (Figure 2). Besides, as mentioned above a new quadruplet c' is observed at 2.33 ppm. These two last resonances c' and e' are characteristic of both a reinitiation of the polymerization by **PEO-2** and a control of the PE segment growth by the dithiocarbamate moiety. The difference in reactivity between **PEO-1** and **PEO-2** during block copolymerization with ethylene can be attributed to the better transfer of propagating radicals PE^\bullet to **PEO-2**, favored by the two aromatic groups, compared to only one in **PEO-1**. This results in better stabilization of the intermediate radical in the well-established RAFT mechanism. Eventually, the starred triplet at 2.39 ppm may stem from a thioether species ($\text{PEO-PE-CH}_2\text{-S-CH}_2\text{-PE-PEO}$),^[44] previously identified as a side product from cross-termination between polymer radicals and intermediate radicals involved in the RAFT polymerization of ethylene.^[39] The better stabilization and therefore the higher concentration of the intermediate radical when **PEO-2** is used might be responsible for the presence of this species. The integration of the corresponding starred signal of the 4 protons (two methylenes) is small (when $a'+e'$ is set to 5, c' is 1 and the starred signal is 0.28). Therefore, this side reactions does not seem to affect the course of the polymerization to a large extent.

The relative integration of the methylene repeating units of the PE block (centered at $\delta = 1.25$ ppm) and of the PEO block (centered at $\delta = 3.48$ ppm) allows for the determination of the molar masses of the PEO-*b*-PE copolymers (Table S1 and Figure 3). The $M_{n,\text{PE}}$ values determined by $^1\text{H NMR}$ are very close to the expected values when **PEO-2** is used (Table S1, entries 10-13). This results in an evolution of the overall block copolymer M_n value versus PE yield which is remarkably close to the theoretical line (Figure 3). As a conclusion, these results confirm the successful chain extension of **PEO-2** into PEO-*b*-PE and the formation of well-defined PE-based block copolymers by RAFT.

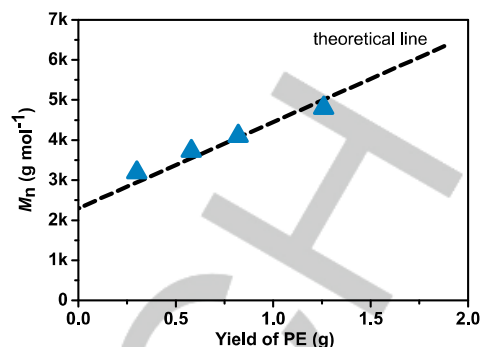


Figure 3. Molar masses of PEO-*b*-PE copolymers from **PEO-2**, determined by $^1\text{H NMR}$ in $\text{TCE}/\text{C}_6\text{D}_6$ (2:1 by volume), versus yield of PE.

The content of the reactor after ethylene polymerization in the presence of **PEO-2** systematically looked like a milky white dispersion. These dispersions were stable (decantation observed after a few days but it was easily re-dispersible by manual shaking). As mentioned above, because of the good solubility of the PEO segment in DMC on the one hand, and the poor solubility of homopolyethylene in DMC on the other hand, we considered that this dispersion could be the result of the self-assembly of the PEO-*b*-PE block copolymers during their formation according to a PISA process.

This motivated us to first perform DLS measurements on experiments carried out with **PEO-2** (i.e., after 2, 4, 6 and 8 hours of polymerization). The corresponding data are provided in the Supporting information (Figures S3-S4). The copolymers were recovered after drying under vacuum at 70 °C for 4 hours. A 1 wt% solution in DMC was then prepared and stirred overnight at room temperature before being sonicated for 30 minutes and finally analyzed by DLS. Part of this dispersion was also dried under the fume hood and the dry extract redispersed in water (1 wt%), sonicated for 30 minutes before being analyzed by DLS. These sample preparations are not expected to affect the particle morphology obtained when the dispersion was collected from the reactor as the crystalline character of the PE block, as supported by DSC analyses ($T_{m,\text{PE}} \sim 106\text{-}112$ °C, Table S1), should “lock” the morphology. This was indeed confirmed by DLS analyses performed directly on the dispersions obtained in DMC after 4 and 8 hours of reaction, which were compared with those of the corresponding samples redispersed in DMC following the above-mentioned procedure (Figure S5).

As shown by the different correlograms from Figures S3 and S4, which are perfectly reproducible over several runs, nano-objects are present both in DMC and water. However, in both cases, the determination of the size of these objects is not consistent over several runs, indicating that the samples contain either several type of objects or objects that are not spherical, or a combination of both. This is what drove us to further investigate these samples in DMC and water with transmission electron microscopy (TEM) and cryogenic TEM (cryoTEM), respectively.

For TEM, an aliquot of the dispersion in DMC was set aside directly at the end of the polymerization, diluted with DMC and deposited on a TEM grid. A picture of the sample obtained after 8 hours of reaction mediated by **PEO-2** (entry 13 in Table S1) is

shown in Figure S6. Different morphologies can be seen on that picture, such as worms or even 2D platelets, the presence of spheres being more difficult to assert. Further comments would however be risky. Indeed, taking into account the nature of the block copolymers (notably the low T_g of the blocks) it would be more relevant to observe these samples in their dispersed state.

Taking advantage of both the water solubility of PEO and the crystallinity of PE, we next investigated the self-organization of these block copolymers in water. CryoTEM observations were performed on the aqueous dispersions prepared as mentioned above, after 2 to 8 hours of reaction (Figure 4). For all the polymerization times, a variety of morphologies including small spheres, worms, small and large 2D platelets are present within the same sample (additional images are available in Figures S7-S10). However, upon increase of the polymerization time, i.e. of the molar mass of the PE block, the fraction of small spheres disappear to the benefit of the higher-order morphologies, the size of which increases. Due to the variety of morphologies observed, the respective fraction of a given morphology is however difficult to determine. In PISA systems, morphology changes are often dictated by increase of the molar mass of the solvophobic block for a fixed molar mass of the solvophilic block.^[29] The expected and clean switch of morphology from spheres to worms to vesicles to 2D platelets is not observed here. The 2D platelets and worm morphologies, particularly after 8 hours of polymerization, are probably favored by the crystalline character of the PE segment.^[45] Indeed, polymerization-induced crystallization-driven self-assembly (PI-CDSA), as recently coined by Manners *et al.*,^[46-47] can be described as a process that successfully merges the best properties of PISA and CDSA of preformed block copolymers exhibiting one crystalline block. CDSA indeed refers to the solution phase behaviour of block copolymers in a selective solvent, where in addition to solvophobic interactions, crystallization of the core forming block influences the self-assembly process.^[48-49] Originally achieved using a living anionic polymerization, examples of PI-CDSA using ring opening metathesis polymerization also exists.^[50]

Previous works from our group showed that PE latex nanoparticles (obtained by convention emulsion radical polymerization) did not crystallize at the temperature of the polymerization (70-80°C) as a result of the nano-confinement of the PE chains but rather during cooling of the PE latex.^[51] In our system, all of the previous analyses may not reflect the nano-organization during polymerization resulting from the PISA process. Indeed, the cooling of the reactor to recover the dispersion may be involved in the formation of the numerous morphologies observed very early in the reaction, by a kind of micellization (during polymerization) and crystallization (during cooling) process.^[52] The formation of micrometer size 2D platelets of polyethylene-*b*-poly(ethylene-*alt*-propylene) block copolymers has for example been shown to be favoured by the crystallization of PE during cooling.^[45] The unexpected visualization of worms after 8 hours when higher-order morphologies were already present at earlier stage of the polymerization may indicate that the higher molar mass of the PE segments after 8 hours induces crystallization during polymerization locking the morphologies upon cooling. It remains anyway difficult to further discuss the self-assembly of the PEO-*b*-PE during polymerization at this

stage. *In situ* characterization methods will better shed light on the underpinning self-assembly mechanism. High pressure cell *in situ* SAXS has indeed recently been used to study polymerization in supercritical CO₂^[53-54] and may be the perfect tool to identify whether the present system is matching the criteria of PI-CDSA. To the best of our knowledge, the present system nevertheless features the very first example of PISA involving ethylene and RAFT, and more generally speaking, RDRP.

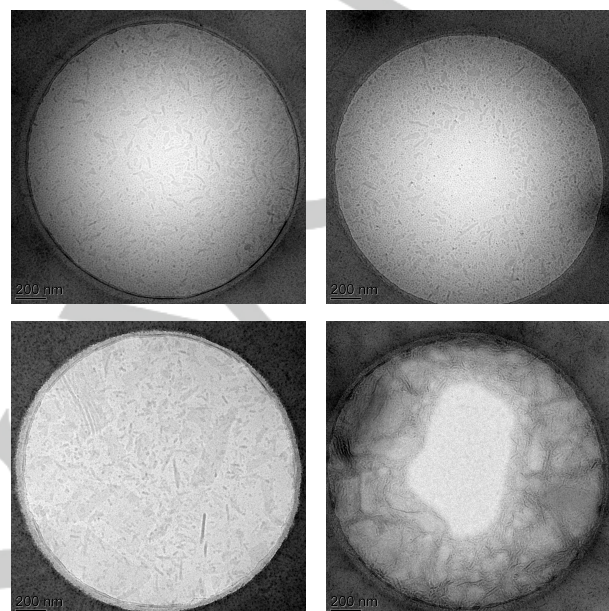


Figure 4. Cryo-TEM images of PEO-*b*-PE dispersions in water obtained after a) 2 hours, b) 4 hours, c) 6 hours and d) 8 hours of polymerization of ethylene in the presence of PEO-2 in DMC at 80 °C and 80 bar.

In conclusion, PEO equipped with dithiocarbamate chain ends were used to mediate the RAFT polymerization of ethylene. Well-defined PEO-*b*-PE block copolymers were formed in DMC when PEO carrying a *N,N*-diphenyl dithiocarbamate chain end was used. The final polymerization medium was a stable dispersion of the targeted block copolymers. Those block copolymers self-assembled into nano-objects upon polymerization of ethylene according to a PISA process. The crystalline nature of the PE segment induced a variety of morphologies including worms. This paper thus describes the first example of PEO-*b*-PE block copolymers formed by RDRP of ethylene and the first ethylene polymerization-induced self-assembly of the resulting block copolymers that are forming stable dispersion in DMC.

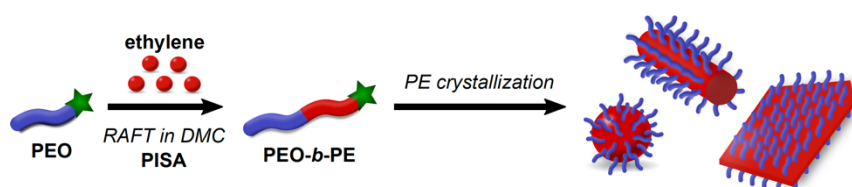
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Keywords: reversible addition-fragmentation chain transfer (RAFT) • block copolymer • ethylene • self-assembly • crystallization

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COMMUNICATION



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First example of PEO-*b*-PE block copolymers formed by RAFT of ethylene and first ethylene polymerization-induced self-assembly of the resulting block copolymers

Ethylene polymerization-induced self-assembly (PISA) of poly(ethylene oxide)-block-polyethylene copolymers via RAFT