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# Ethylene Coordinative Chain Transfer Polymerization-Induced Self-Assembly (CCTPISA)

Nicolas Baulu,<sup>a,b</sup> Marvin Langlais,<sup>a,c</sup> Pierre-Yves Dugas,<sup>a</sup> Julien Thuilliez,<sup>b</sup> François Jean-Baptiste-dit-Dominique,<sup>b,c</sup> Muriel Lansalot,<sup>a</sup> Christophe Boisson,<sup>\*,a,c</sup> Franck D'Agosto<sup>\*,a,c</sup>

**Abstract:** Block copolymers based on ethylene (E) and butadiene (B) were prepared using the *ansa*-bis(fluorenyl) complex  $\{\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_9)_2\text{Nd}(\text{BH}_4)_2\text{Li}(\text{THF})_2\}$  in combination with (*n*-Bu)(*n*-Oct)Mg (BOMAG) as a chain transfer agent. The diblock copolymers incorporating a soft poly(ethylene-co-butadiene) segment, called EBR for Ethylene Butadiene Rubber, and a hard polyethylene (PE) one were obtained by simply adjusting the different feeds of monomers during the polymerization. The soluble EBR block was formed first by feeding the catalytic system dissolved in toluene at 70 °C with a mixture of ethylene and butadiene (E/B molar ratio = 80/20). Then the feeding was stopped leading to the consumption of a large part of the residual monomers. The reactor was finally fed with ethylene to form the PE block. By varying the molar mass of the latter, it is shown that the resulting soft-*b*-hard block copolymers can self-assemble simultaneously to the growth of the PE block in agreement with a polymerization-induced self-assembly (PISA) mechanism. The self-assembly is discussed considering the reaction conditions, the crystallization of the PE block and the polymerization mechanism involved.

## Introduction

Polymerization-induced self-assembly (PISA) has recently been the topic of a tremendous number of papers and reviews,<sup>[1-11]</sup> and featured in several journal special issues.<sup>[12-13]</sup> PISA consists in first producing well-defined polymer chains by a living polymerization technique in a good solvent. These soluble chains are then further extended with either a solvophobic (emulsion)<sup>[14]</sup> or solvophilic (dispersion)<sup>[15]</sup> monomer to lead to the formation of a solvophobic block. Upon the growth of the solvophobic block, the resulting solvophilic-solvophobic block copolymers can self-assemble into nanoparticles of various morphologies.<sup>[16]</sup> PISA is thus a new, simple and extremely powerful tool to produce block

copolymers and self-assemble them at much higher solids content (up to 50 wt%)<sup>[17]</sup> that the ones generally targeted when preformed block copolymers are assembled with co-solvent techniques.<sup>[18-19]</sup> PISA finds its origins in older living anionic polymerization works in which living poly(*tert*-butylstyrene) chains were chain-extended with styrene or divinylbenzene in *n*-hexane to produce polystyrene particles under dispersion polymerization conditions.<sup>[20]</sup> PISA has been largely applied to reversible-deactivation radical polymerization (RDRP) techniques, originally<sup>[21]</sup> and mainly since then via the reversible addition-fragmentation chain transfer (RAFT) process.<sup>[22-23]</sup> PISA is conceptually transposable to any living polymerization techniques. Pioneered with RDRP using RAFT by Ferguson *et al.*,<sup>[21]</sup> PISA has indeed also been recently applied to non-radical based polymerization techniques<sup>[24]</sup> such as ring opening metathesis polymerization,<sup>[25-27]</sup> anionic ring opening polymerization of *N*-carboxyanhydride<sup>[28-29]</sup> or Ni-catalyzed isocyanide,<sup>[30]</sup> or allene polymerization.<sup>[31]</sup>

To the best of our knowledge the realm of polyolefins (PO) has not been investigated in the context of PISA although olefin polymerization in dispersed media can be successful.<sup>[32]</sup> Relying on our recent advances in the controlled radical polymerizations of ethylene,<sup>[33-36]</sup> we showed that this monomer too could be involved in PISA to generate not only unique poly(ethylene oxide)-*b*-polyethylene (PEO-*b*-PE) block copolymers by RAFT starting from a dithiocarbamate functionalized PEO, but also original non-spherical PEO-*b*-PE particles.<sup>[37]</sup> The possibility to access all-PO block copolymers is really attractive as PO are the most produced polymers industrially.<sup>[38]</sup> Indeed, obtained from a very narrow set of easily available monomers (i.e. ethylene, propylene,  $\alpha$ -olefins, dienes), PO achieve unique properties (thermal and chemical stability, mechanical properties, elasticity) that cannot be found in other polymers. These properties are however sometimes difficult to combine in the same chain unless they are carried by polymer segments in a block copolymer chain. Such block copolymer chains would favor a broader range of applications. This combination of properties must be considered taking into account industrially available polymerization techniques. Coordinative chain transfer polymerization (CCTP)<sup>[39]</sup> is a controlled polymerization analogous to a RAFT process for radical polymerization.<sup>[40]</sup> A chain transfer agent (CTA) based on a main group metal complex is used to reversibly exchange the produced chains on the transition metal complex used as a catalyst. CCTP is indeed one of the techniques used in the industry for the production of olefin block copolymers via a solution high temperature process (INFUSE™). The obtained

a. Dr. N. Baulu, Dr. M. Langlais, P.Y. Dugas, Dr. M. Lansalot, Dr. C. Boisson, Dr. F. D'Agosto, Université de Lyon, Université Lyon 1, CPE Lyon, CNRS UMR 5128, Laboratoire CP2M, Équipe PCM, 69616 Villeurbanne, CEDEX, France  
E-mail: [franck.dagosto@univ-lyon1.fr](mailto:franck.dagosto@univ-lyon1.fr); [christophe.boisson@univ-lyon1.fr](mailto:christophe.boisson@univ-lyon1.fr)

b. Dr. J. Thuilliez, Dr. F. Jean-Baptiste-dit-Dominique, Manufacture des pneumatiques Michelin, 23 Place des Carmes Dechaux, 63040 Clermont-Ferrand, France

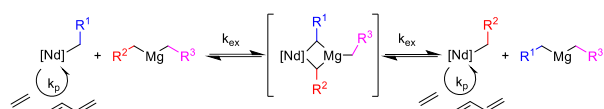
c. Dr. M. Langlais, Dr. F. Jean-Baptiste dit Dominique, Dr. C. Boisson, Dr. F. D'Agosto, ChemistLab, Michelin CP2M ICBMS joint Laboratory 69616 Villeurbanne, France.

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

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copolymers are composed of hard crystalline and soft rubbery segments.<sup>[41]</sup>

In collaboration with the Michelin company, we developed new polyolefin elastomers obtained by solution copolymerization of ethylene (E) and butadiene (B) with the lanthanidocene complex  $\{\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)_2\text{Nd}(\text{BH}_4)_2\text{Li}(\text{THF})\}_2$  used in presence of  $(n\text{-Bu})(n\text{-Oct})\text{Mg}$  (BOMAG) as an alkylating agent.<sup>[42-43]</sup> Obtained in organic solvent such as toluene, these soluble polymers were named EBR for Ethylene Butadiene Rubber. They feature *trans*-1,4-butadiene, vinyl-butadiene and 1,2-cyclohexane moieties. We indeed recently showed that the resulting system is controlled. In this system, BOMAG acts as a reversible CTA according to a controlled CCTP process.<sup>[44]</sup> Well-defined poly(ethylene-co-butadiene) can thus be easily prepared according to a catalytic chain transfer copolymerization (CCTcoP) process (Scheme 1).



Scheme 1. Coordinative chain transfer copolymerization (CCTcoP) of ethylene and butadiene with a Nd-based complex in the presence of a dialkylmagnesium chain transfer agent.

In the case of the homopolymerization of ethylene mediated by neodymium complexes<sup>[45-48]</sup> and conducted in toluene,<sup>[49-51]</sup> the fast and reversible chain transfer between neodymium and magnesium leads to the formation of well-defined dipolyethylenemagnesium by controlled CCTP. The range of temperature for which the polymerization is controlled (*i.e.*, few to no H elimination) is generally limited to 80 °C. The maximum average molar masses of well-defined PE obtained under these conditions are indeed dictated by its crystallization in the polymerization medium. When higher molar masses are targeted, PE crystallization occurs and is accompanied by the loss of the polymerization control due to the reduction of chain mobility.

Nevertheless, the ability of lanthanidocene catalysts to operate according to a CCTP process for both the synthesis of soft EBR and hard PE segments sets the path for the preparation of unprecedented EBR-*b*-PE block copolymers. The possibility to control both the copolymerization of E and B and the homopolymerization of E with the same  $\{\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)_2\text{Nd}(\text{BH}_4)_2\text{Li}(\text{THF})\}_2/\text{BOMAG}$  catalytic system<sup>[44]</sup> drove us to examine in the present work the preparation of such new EBR-*b*-PE block copolymers in toluene. In the course of these studies and when screening different molar masses for the PE block, further attention was paid to the potential self-assembly of the EBR-*b*-PE block copolymers during the growth of the PE block. This work thus aims at extending, for the very first time, the concept of PISA to the realm of polyolefins via a catalytic chain transfer polymerization-induced self-assembly (CCTPISA) process.

## Results

The controlled behavior of the copolymerization of ethylene with butadiene using  $\{\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)_2\text{Nd}(\text{BH}_4)_2\text{Li}(\text{THF})\}_2/\text{BOMAG}$  catalytic system was recently demonstrated.<sup>[44]</sup> We thus first targeted a well-defined EBR with a number-average molar mass ( $M_n$ ) of 3800 g mol<sup>-1</sup> by copolymerizing ethylene and butadiene (80/20 molar ratio) in toluene at 70 °C (Table 1, run 1). Before switching the feed to pure ethylene, the reactor was isolated from the 80/20 ethylene/butadiene feed once the targeted quantity of monomers was consumed. The pressure then dropped from 4 bar to 2.8 bar. The reactor was then repressurized to 4 bar with pure ethylene. The remaining B was thus rapidly consumed in this second polymerization step. E was fed into the reactor to form four different PE segments with targeted molar mass of 1000, 3000, 4000 and 8000 g mol<sup>-1</sup>. Five copolymers were thus obtained after recovery from the polymerization reactor and are presented in Table 1.

Table 1: Characteristics of the starting EBR copolymer and the different EBR-*b*-PE block copolymers

Run	Targeted $M_n$ for PE block (g mol <sup>-1</sup> ) <sup>1</sup>	Mass of polymer (g)	$M_n$ targeted (g mol <sup>-1</sup> ) <sup>a</sup>	Polymerization time	$M_n$ SEC (g mol <sup>-1</sup> ) <sup>b</sup>	$\bar{D}$	$T_g^c$ (°C)	$T_m^c$ (°C)	$X^c$ (%)	E/B (mol %) <sup>e</sup>	B unit (2,1 insertion) (mol%) <sup>e</sup>	B unit (1,4 insertion) (mol%) <sup>e</sup>	Cyclohexyl ring (mol%) <sup>e</sup>	E unit (mol%) <sup>e</sup>
1	0	3.8	3800	2h40 <sup>f</sup>	3900	2.1	-45	-	0	76.1/23.9	12.1	6.8	9.5	71.6
2	1000	5.1	5100	3h36	5200	2.2	-40	-	1	79.3/20.7	9.7	5.7	9.0	75.6
3	3000	7.3	7300	3h45	8200	2.2	-38	105-120	11	84.4/15.6	6.9	4.1	6.6	82.4
4	4000	7.4	7400	2h12 <sup>g</sup>	8800	1.8	-44	115-125	20	87.9/12.1	4.7	3.0	5.8	86.5
5	8000	12.9	12900	3h55	19000	4.2	-40	132	45	93.8/6.2	2.2	1.4	2.8	93.6

Copolymerizations were conducted in toluene at 70 °C (200 mL),  $[\text{Nd}] = 63 \mu\text{mol L}^{-1}$ ,  $[\text{BOMAG}] = 2.5 \text{ mmol L}^{-1}$ ,  $\text{Mg}/\text{Nd} = 40$ ,  $P = 4 \text{ bar}$ . <sup>a</sup> $M_{n\text{targeted}}$  = Mass of copolymer recovered/nb of moles of BOMAG used. <sup>b</sup> Obtained by HT-SEC using a universal calibration. <sup>c</sup> Determined by DSC.  $X$  = Crystallinity. <sup>d</sup> Determined by DSC using  $\Delta H_f = 293 \text{ J g}^{-1}$  for 100% crystalline PE. <sup>e</sup> Determined by <sup>1</sup>H NMR analyses of the copolymers. <sup>f</sup> Taken after the pressure was decreased to 2.8 bar. <sup>g</sup> Resulting from a possible higher concentration of catalyst involved.

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The relatively high dispersity value obtained for run 1 ( $\bar{D} = 2.1$ ) was not unexpected. Indeed, a relatively low chain transfer constant to BOMAG resulting in a time delay to balance the set of equilibrium between active and dormant polymeric species (Scheme 1) was already observed and discussed for this catalytic copolymerization system.<sup>[44]</sup> The system remains living as attested by run 2, in which the chain extension of the EBR produced in run 1 is indeed observed as shown by the increased  $M_n$  (5200 g mol<sup>-1</sup>) while the dispersity remains similar ( $\bar{D} = 2.2$ ). In addition, the expected lone  $T_g$  observed at -45 °C for the starting EBR is still observed in the polymer obtained in run 2, although slightly higher ( $T_g$  of the starting EBR, -40 °C), yet now accompanied by a melting phenomenon for which the temperature remains however hard to determine (See Figure S2). As mentioned above, after the synthesis of the EBR first block, for simplicity's sake and to avoid expensive vacuum cycles, the feed of E/B comonomers is simply stopped and a pure ethylene feed is applied once a pressure of 2.8 bar is reached in the reactor. This leads to a rapid consumption of the remaining butadiene when forming the formed PE block that is additionally likely too short to easily observe the  $T_m$  in this case. When longer PE segments are targeted (runs 3 to 5), a glass transition temperature at ca. -40 °C, characteristic of a soft elastomeric EBR segment, is still systematically observed. However, the presence of a melting temperature (between 105 and 125 °C, Figure S2) is now clearly visible and increases with the molar mass of PE block in the final copolymer (Figure 1).

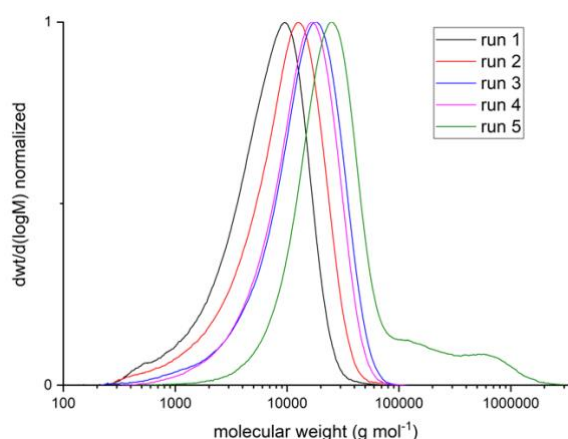


Figure 1. HT-SEC traces of the starting EBR (Table 1, run 1) and its chain extensions with ethylene targeting different molar masses (Table 1, runs 2-5).

These thermal properties are strong indications that the targeted structures are indeed obtained. These results together with the monodispersed molar mass distribution observed for run 2 to 4 (Figure 1) clearly evidence the successful chain extension of EBR with ethylene and the formation of new EBR-*b*-PE block copolymers incorporating both (elastomeric) soft and hard (crystalline) segments. The molar mass distribution obtained for run 5 also confirmed a successful chain extension although the concomitant formation of high molar mass chains is visible showing that the control of the polymerization started to be impacted in that case.

The composition drift discussed above, induced by the operating conditions used for the formation of the second block, can easily explain the microstructure of the obtained chains, as determined by <sup>1</sup>H NMR analyses (Figure S1 and Table 1). The microstructure expected for an EBR<sup>[42-43]</sup> prepared with an 80/20 E/B molar feed exhibiting 2,1- and 1,4-inserted butadiene units as well as cyclohexyl moieties and ethylene units is obtained for run 1. This confirms that the small composition drift that takes place when the reactor is isolated and before it is pressurized with pure E does not impact the overall microstructure of the EBR. When chain extension with E takes place, the increase of E content is observed as expected.

The final medium for the copolymerization of E and B under the conditions used here was homogenous and clear as EBRs are fully soluble in toluene at 70 °C (Figure 2, run 1). In our hands and under similar reactions conditions, homopolymerization of E with the same catalytic system leads to a homogenous system up to a molar mass of ca. 2000 g mol<sup>-1</sup> for the PE chains. Indeed, as mentioned in the introduction, the crystallinity of PE prevents to target high molar masses. The precipitation observed in this case deprives the system from its PE-Mg-PE macromolecular chain transfer agents (macroCTA) and the control of the CCTP is then lost. In this situation indeed, the polymerization rate strongly increases as conventional coordination-insertion polymerization takes place, followed by a rapid deactivation of the catalyst, and high molar mass PE chains are produced.<sup>[49, 52]</sup> Owing to the precipitation of the PE chains, the final polymerization medium is a turbid dispersion in which decantation quickly occurs when stirring is stopped. The situation is quite different in the present system where an EBR is chain-extended with a PE block. Indeed, even though the growing PE block is expected to reach a molar mass above which crystallization will occur, the EBR segment might help the corresponding block copolymers to self-assemble into stable nanoobjects as usually observed in a PISA process. This is indeed what is first visually and qualitatively seen after cooling of the final reaction media (Figure 2) for the different runs presented in Table 1. While run 2 does not exhibit any turbidity - probably because the short PE block contains a few B units and thus remains soluble, runs 3 to 5 are stable dispersions (no precipitation) exhibiting a turbidity, which becomes more and more significant as the molar mass of the PE block increases. It is worth mentioning here that the turbidity is observed before cooling the reactor for runs 4 and 5 while it only takes place on cooling for run 3 (no turbidity before and after cooling for run 2). This turbidity is associated with the self-assembly of the formed block copolymers. These data are a strong indication that the control of the polymerization does not seem to be prevented by the self-assembly as increasing molar mass of PE are reachable (runs 4 and 5) although the control of the polymerization seems to be impacted for run 5 as mentioned above. Conversely to the homopolymerization of ethylene, the appearance of the turbidity in the polymerization medium is not accompanied by an increase in activity.<sup>[47]</sup> However, after consumption of about 6 g of ethylene a sudden drop in activity (from 300 kg mol<sup>-1</sup> h<sup>-1</sup> to 140 kg mol<sup>-1</sup> h<sup>-1</sup>) is observed (not shown) after which the activity reaches a plateau. These observations strongly support that the polymerization takes place in the formed particles where the catalyst must now be located, and still according to a CCTP mechanism. Besides, the data show that self-assembly of the

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block copolymers occurs at the polymerization temperature and/or on cooling when the molar mass of the PE is high enough. The resulting objects would then be composed of a hard PE core decorated with a soft EBR shell. This prompted us to investigate whether the self-assembly was indeed confirmed by studying by DLS and TEM of runs 1-4. Considering the loss of control observed in Run 5, this sample was not further considered although it gives rise to a stable dispersion.

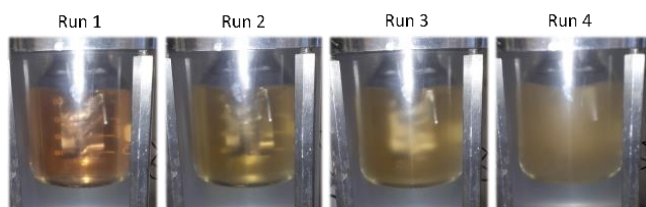


Figure 2. Photos of the reactor at the end of the polymerization for runs 1 to 4 (Table 1) after cooling.

Diluted samples of runs 1 and 2 did not give any signal when studied by DLS in toluene confirming the absence of any nanoorganization of the chains in these samples, even at ambient temperature. On the contrary, DLS analyses of runs 3 to 4 do exhibit a signal (Figure S3) showing the presence of very large size objects ( $> 2$  nm). Soft sonication using an ultrasound water bath of the samples before analysis however evidences the presence of smaller objects (160 nm for run 4 in Figure S3), indicating that the objects isolated at the end of the polymerization are aggregates.

The samples from runs 3 and 4 were then further characterized by TEM. The formation of non-spherical nanoobjects is clearly confirmed for runs 3 and 4 (Figure 3). Indeed, for runs 3 and 4 worm-like morphologies can easily be identified. The worms are a ca. 100 nm length for a ca. 10 nm diameter. The visualization of non-spherical morphologies makes *a posteriori* the DLS values difficult to consider.

## Discussion

We showed above that EBR-*b*-PE block copolymers with different molar masses for the PE block can be formed by taking advantage of the controlled behavior of the CCTP, which allows chain extension of a preformed EBR. As the molar mass of the PE block increases, self-assembly occurs during polymerization or after cooling leading to stable EBR-*b*-PE dispersions. DLS and TEM analyses confirmed an organization at the nanometer scale of the block copolymers. As such, it is safe to say that this system obeys a PISA process.

It is however important to keep in mind that the self-assembly process of such block copolymers might be more complex than the already complicated one observed for most PISA systems based on diblock copolymers. If after deactivation of the medium with methanol, EBR-*b*-PE block copolymers are indeed obtained, during polymerization and according to the CCTP mechanism (Scheme 1) the macromolecular species involved are (i) a

majority of EBR-*b*-PE-Mg-PE-*b*-EBR chains acting as macroCTA and a small number of EBR-*b*-PE chains connected to a Nd center.

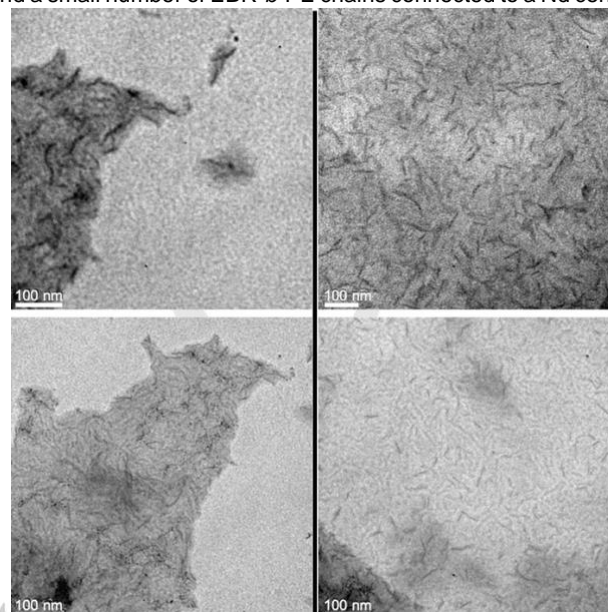


Figure 3. TEM analyses of samples from runs 3 (left) and 4 (right) (Table 1).

The self-assembly observed through the appearance of turbidity during the polymerization is thus reflecting the concomitant chain extension and the self-assembly of these block copolymer species. The self-assembly phenomenon does not prevent the CCTP to efficiently operate after the formation of the nanoobjects. However, the decrease in activity observed in run 5 once a PE molar mass of ca. 6000 g mol<sup>-1</sup> has been reached might show that the diffusion of ethylene inside the particles could be modified. The small population of high molar mass observed in Figure 1 for run 5 might also be consistent with the difficulty of macromolecular species to keep on exchanging when the molar mass of the PE block increases and to maintain the control of the polymerization inside the particles.

The crystallinity of the particles during the polymerization might explain the above-mentioned results and may reflect that not only self-assembly but also crystallization inside the particles is taking place. Besides, it is also interesting to note that the morphology observed for the range of PE molar masses investigated here are limited to worms. Indeed, spheres or vesicles are not observed. In PISA systems<sup>[22]</sup> or for self-assembly of block copolymers in a selective solvent,<sup>[18]</sup> switches of morphology from spheres to worms to vesicles to 2D platelets are observed and driven by the increase of the molar mass of the solvophobic block for a fixed molar mass of the solvophilic block. The worm morphology is probably favored by the highly crystalline character of the PE segment (very linear PE chains here)<sup>[53-54]</sup> as already observed for less crystalline PE block obtained by RAFT-mediated PISA of ethylene (slightly branched PE chains).<sup>[37]</sup> Indeed, formation of worms and 2D platelets were depicted in the particular case of crystallization-driven self-assembly (CDSA) of preformed block copolymers with one crystalline block in a selective solvent of the other block.<sup>[55]</sup> Block copolymer worms were further obtained by

living CDSA<sup>[56]</sup> in a selective solvent, starting from a dispersion of preformed uniform block copolymer crystallite seeds.<sup>[57]</sup> Those seeds serving as initiator for the co-crystallization of added block copolymer unimers with one crystalline block of the same nature of the seed core. A scalable version of these strategies that originally required preformed block copolymers and highly diluted conditions is the combination of CDSA and PISA (coined PI-CDSA), or PI-CDSA in the presence of crystallite seeds that leads to living PI-CDSA.<sup>[58]</sup> In all these works however, the polymerization and the self-assembly and thus crystallization of one of the block take place at room temperature. In our system, the implication of CDSA cannot be ruled out. The polymerization takes place at 70 °C and the medium is then cooled down to room temperature. It is understandable that for low molar mass PE block as in run 3, the turbidity only appears on cooling and that in this case, the contribution of CDSA processes to the formation of the observed worms is strong. CDSA could also be involved when turbidity is observed during polymerization step (runs 4 and 5). Nevertheless, as the molar mass of PE increases, the quality of toluene as a solvent should decrease and even if no crystallization takes place, self-assembly according to PISA during the polymerization might occur, followed by crystallization either during the reaction or on cooling. In conclusion, it remains difficult to further discuss the self-assembly of the EBR-*b*-PE block copolymers during polymerization (PISA, CDSA, PISA and CDSA or PI-CDSA) at this stage. As in the case of our previous studies on RAFT-mediated PISA of ethylene,<sup>[22]</sup> the ethylene CCTPISA would require additional investigation, such as *in situ* SAXS which nevertheless remain difficult to implement,<sup>[59-60]</sup> to better shed light on the underpinning self-assembly mechanism.

## Conclusion

In the present paper, coordinative chain transfer (co)polymerization (CCT(co)P) of ethylene and butadiene was implemented in toluene at 70 °C in the presence of  $\{\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)_2\text{Nd}(\text{BH}_4)_2\text{Li}(\text{THF})\}_2/(n\text{-Bu})(n\text{-Oct})\text{Mg}$  catalytic system. The known controlled behaviors of both the copolymerization of ethylene and butadiene and the homopolymerization of ethylene were advantageously employed in the same reactor to produce poly(ethylene-*co*-butadiene)-*b*-polyethylene block copolymers for the first time by CCTP. Under appropriate conditions, this leads to a stable and ready to use dispersion of anisotropic polyolefin block copolymer nanoparticles. The underpinning self-assembly mechanism leading to this morphology cannot be fully elucidated at this stage although self-assembly does occur during polymerization and upon the growth of the polyethylene segments as shown by the turbidity observed and in agreement with a polymerization-induced self-assembly (PISA) mechanism. This PISA system is mediated by catalytic coordination-insertion polymerization and opens the way to the design of original block copolymers and organic nanoparticles based on polyolefins, including by the use of original polymerization switch such as from anionic to CCTP.<sup>[61]</sup>

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## Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. N.B. and Ma.L performed the experiments and carried out the characterizations. P.Y.D performed TEM analyses. All authors discussed the results and commented on the manuscript. F.D. and C.B supervised and designed the research. F.J.B.D. and J.T. co-supervised the research. F.D. Mu.L. and C.B. wrote the manuscript with suggestions from all the authors.

## Experimental section

Experimental details (experimental information and materials, characterization techniques employed such as nuclear magnetic resonance (NMR), high-temperature size exclusion chromatography (HT-SEC), differential scanning calorimetry (DSC), dynamic light scattering (DLS), transmission electron microscopy (TEM) and copolymer synthesis procedures can be found in Supporting Information.

**Keywords:** ethylene • butadiene • block copolymers • CCTP • PISA

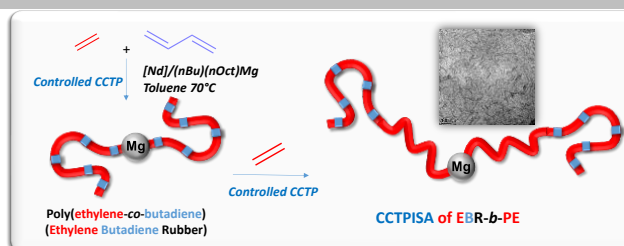
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## RESEARCH ARTICLE

Ethylene coordinative chain transfer polymerization-induced self-assembly is performed by chain extending poly(ethylene-co-butadiene) living chains in toluene in the presence of ethylene and a Nd-based catalyst.



*N Baulu, M. Langlais, P.-Y. Dugas, J. Thuilliez, F. J.-B. dit Dominique, M. Lansalot, C. Boisson,\* F. D'Agosto\**

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