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► **To cite this version:**

Nicolas Baulu, Marvin Langlais, Robert Ngo, Julien Thuilliez, François Jean-Baptiste-Dit-Dominique, et al.. Switch from Anionic Polymerization to Coordinative Chain Transfer Polymerization: a Valuable Strategy to Make Olefin Block Copolymers. *Angewandte Chemie International Edition*, 2022, 61 (26), pp.e202204249. 10.1002/anie.202204249 . hal-03722001

HAL Id: hal-03722001

<https://hal.science/hal-03722001v1>

Submitted on 13 Jul 2022

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RESEARCH ARTICLE

Switch from Anionic Polymerization to Coordinative Chain Transfer Polymerization: a Valuable Strategy to Make Olefin Block Copolymers

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Abstract: Anionic polymerization of butadiene or/and styrene is performed with lithium initiators functional or not. The polymer chains are subsequently transferred to magnesium. The resulting polymeryl-magnesium compounds were combined with $\{(Me_2Si(C_{13}H_8)_2)Nd(\mu-BH_4)[(\mu-BH_4)Li(THF)]\}_2$ metallocene complex to act as macromolecular chain transfer agent (macroCTA) in coordinative chain transfer polymerization (CCTP) of ethylene (E) or its copolymerization (CCTcoP) with butadiene (B). Block copolymers were produced for the first time by this switch from anionic polymerization to CCTP. Hard and soft blocks such as PB, polystyrene (PS), poly(styrene-co-butadiene) (SBR) obtained by anionic polymerization and PE or poly(ethylene-co-butadiene) (EBR) produced by CCT(co)P were combined and the corresponding structures were characterized.

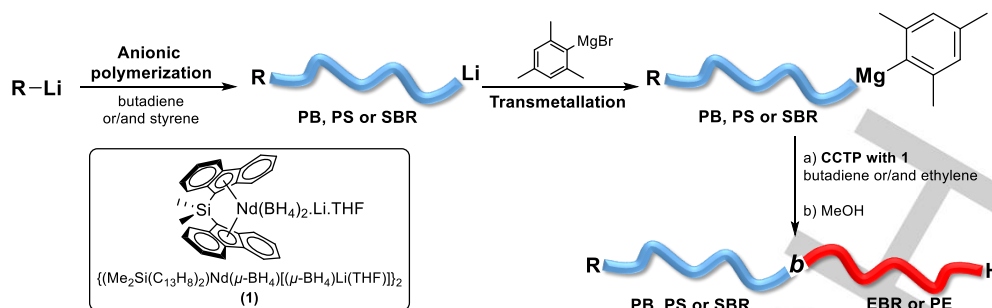
Introduction

Block copolymers are ubiquitous materials in polymer science.^[1–3] They combine the characteristics of the different blocks leading to original properties. For instance, they can self-assemble to form nanostructured films or nanoparticles for electronic and medical applications. Block copolymers can find application in the industry as compatibilizing or stabilizing agents and thermoplastic elastomers.

Polyolefins (POs) are the most important class of plastic. However, the preparation of block copolymers based on PO remains challenging. A functional group can be installed at PO chain-ends and a subsequent block can be formed by chain extension via anionic or radical polymerization.^[4–7] A limitation of this process might be the isolation of the functional PO macromolecular initiator. Reversible deactivation radical polymerization (RDRP) has proved to be a very powerful tool to produce block copolymers. The recently developed RDRPs of ethylene now allows to access block copolymers and more complex architectures based on ethylene.^[8–16] Industrially however, these strategies are not mature enough to be implemented efficiently. Indeed, the vast majority of POs are obtained by coordination-insertion polymerization, the catalytic system being obviously the industrially preferred one. In order to synthesize PO block copolymers, living coordination-insertion polymerization of olefins, although not catalytic, has been widely investigated alone^[17] or in

combination with anionic polymerization. In this last case, block copolymers were obtained via the switch from anionic to coordination-insertion polymerization by transferring the anionic chains to a titanium or vanadium center. Polyethylene or polypropylene block was then produced by living polymerization in a second step.^[18–21]

The living nature in these systems is exploited to design olefin block copolymers considered as precision POs. The associated main limitation for their production is that one active metal center is required per chain produced. This has been alleviated in coordinative chain transfer polymerization (CCTP). CCTP is based on a reversible degenerative transfer between the active site on a transition metal and a main group metal or zinc used in excess as chain transfer agent (CTA).^[22] The rapid and constant exchange of the chain from the active center used in catalytic amount and on which propagation takes place to the CTA ensures the simultaneous growth of a large number of polymer chains per active metal center. The pseudo-living nature of these systems has been exploited by researchers at Dow Chemical to produce in a series of two reactors block copolymers based on low-density and ultra-low density PE segments.^[23] The concept of CCTP was also extended to chain shuttling polymerization. Here, in the same polymerization medium, Hf-based and Zr-based complexes are combined with a common CTA, namely diethylzinc, to selectively homopolymerize ethylene on Zr and copolymerize ethylene and octene (Oct) on Hf leading to PO multiblock copolymers with hard (PE) and soft (P(E-co-Oct)) segments.^[24] Besides, dipolyethylenylmagnesium synthesized by CCTP and used in conjunction with $Nd(BH_4)_3(THF)_3$ allowed the *trans*-selective isoprene polymerization to produce block copolymers with polyethylene and *trans*-polyisoprene segments.^[25] Recently, Lee and coll. realized that di-hexylzinc was able to initiate an anionic polymerization of styrene in the presence of *n*-butyllithium (*n*BuLi) and N,N,N',N'-tetramethylethylenediamine (TMEDA) although side initiation with *n*BuLi was taking place.^[26] They extrapolate this result to the reactivation of PO chains produced by CCTP mediated by organometallic zinc compounds to implement the switch from CCTP to anionic polymerization and produce PO-*b*-PS^[26] and PS-*b*-PO-*b*-PS block copolymers.^[27] As shown in the model experiments conducted with molecular dialkylzinc, this strategy is however associated with the formation of homopolymer formed during the anionic polymerization.



Scheme 1. General description for the preparation of diblock copolymers based on successive anionic polymerization and coordination chain transfer polymerization (CCTP).

CCT(co)P has also been reported when using various dialkylmagnesium compounds as CTAs.^[28–30] In these systems, Nd-based catalysts are preferred and the produced PO chains are linked to a Mg center. We besides have shown that the catalyst $\{(\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)_2)\text{Nd}(\mu\text{-BH}_4)[(\mu\text{-BH}_4)\text{Li}(\text{THF})]\}_2$ (**1**) (Scheme 1)/*n*-butyl-*n*-octylmagnesium (BOMAG) enables CCTcoP of ethylene and butadiene.^[31] The resulting copolymers indeed feature ethylene units, *trans*-1,4 and 1,2 butadiene units and cyclohexyl moieties formed via an intramolecular cyclization mechanism.^[31,32] This peculiar microstructure leads to original properties and the development of a new class of poly(ethylene-co-butadiene) rubber called ethylene butadiene rubber (EBR). Among the different strategies to produce dialkylmagnesium compounds, transmetallation of alkyl group from lithium to magnesium has been proposed.^[33,34] The preparation of macromolecular Grignard reagents has also been depicted by reaction of polystyryllithium with magnesium bromide.^[35] In the present communication, we anticipated that taking advantage of anionic polymerization, various macromolecular anions bound to Li could undergo transmetallation in the presence of an adequately chosen Grignard compound to produce macromolecular CTAs (macroCTA). The use of these macroCTAs to mediate ethylene CCTP and CCTcoP of ethylene and butadiene in the presence of **1** would then lead to unprecedented block copolymers by switching from anionic to CCTP for the first time. A particular care was taken to conduct all these reactions without purifying steps in order to access the final structure in an industrially viable way. Anionic polymerization of butadiene and styrene is performed in a first step and the polymer chain is then transferred to magnesium in order to produce macroCTAs based on polybutadiene (PB), polystyrene (PS) and poly(styrene-co-butadiene) (SBR). The macroCTAs have been used in combination with the complex $\{(\text{Me}_2\text{Si}(\text{C}_{13}\text{H}_8)_2)\text{Nd}(\mu\text{-BH}_4)[(\mu\text{-BH}_4)\text{Li}(\text{THF})]\}_2$ to prepare block copolymers with PE and EBR segments.

Results and Discussion

Mesitylmagnesium bromide (MesMgBr) was used for transmetallation reactions performed in this study. The choice of this Grignard reagent is based on our previous studies that showed that the Nd complex does not initiate polymer chain when combined with mesitylmagnesium compounds.^[36] If transmetallation performed after an anionic polymerization is successful, this feature would allow to resume the polymerization

of ethylene or the copolymerization of ethylene and butadiene exclusively from the polymer formed during the anionic step to achieve clean block copolymers as shown in Scheme 1.

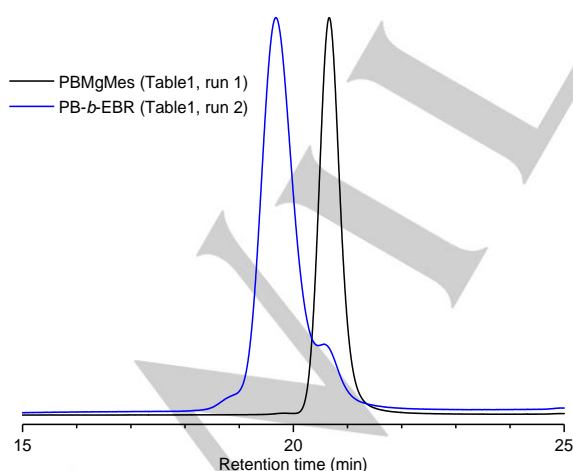
Anionic polymerizations of B were performed in toluene with *n*BuLi as initiator and targeting a molar mass of about 10000 g mol^{-1} ($\text{B/Li} = 185$). An excess of MesMgBr ($\text{Mg/Li} = 1.2$) was then poured directly into the reactor at the end of the polymerization. The turbidity observed at this time is consistent with the expected precipitation of LiBr salts (Figure S1). As shown in Table 1, run 1, the features of the isolated polymer are in agreement with a living anionic polymerization ($\mathcal{D} = 1.06$) and the obtained number average molar mass (M_n) of 11900 g mol^{-1} matched the targeted one (10000 g mol^{-1}). Without any purification step, the obtained suspension containing the targeted PBMgMes macroCTA is directly utilized for the copolymerization of E and B by CCTP (Table 1, runs 2-3). An excess of MesMgBr was used for the transmetallation reaction and that the neodymium complex was also contacted with MesMgBr for the CCTP step. Actually the addition of MesMgBr permits to solubilize the Nd complex and to scavenge impurities without impacting the control of the polymerization. Copolymerizations were performed at 80°C in the presence of the complex **1** under 3.5 bars pressure (E/B molar ratio of 80/20). The monomer consumption is followed by the pressure drop in the monomers reservoir. To be able to easily conclude on a successful chain extension, the copolymerization was planned to be stopped when the monomer consumption corresponded to a M_n for the EBR block equivalent to that of the starting PB block. The observed pressure drop indeed showed that the copolymerization was taking place. The SEC traces of the precipitated polymer is shifted toward higher molar masses compared to that of the PB block (Figure 1). The obtained M_n of 23800 g mol^{-1} and \mathcal{D} of 1.13 (Table 1, run 2) are fully consistent with a successful chain extension via CCTcoP. SEC analyses also show that a small fraction of PB chains is not reinitiated (Figure 1) and are probably dead PB chains formed during the transmetallation process. The NMR analyses of the block copolymers shows characteristic signals of PB and EBR blocks (Figure S2) in agreement with the expected microstructure (Table S1). Finally, DSC analysis of the block copolymer shows glass transition temperatures at -91°C for the PB block and -33°C for the EBR block (Figure S3). These results are fully consistent with the formation of PB-*b*-EBR diblock copolymers and further show that there is no limitation to successfully conduct chain extension via CCTcoP in presence of residual LiBr salt formed after transmetallation step.

Table 1. Polymerization data of polymers used and obtained for the targeting synthesis of PB-*b*-EBR or PS-*b*-EBR diblock copolymers.

Run	Polymer	Yield (g)	$M_n^{\text{theo [c]}}$ (g mol ⁻¹)	$M_n^{\text{SEC [d]}}$ (g mol ⁻¹)	\bar{D} [d]	$T_g^{\text{block 1 [e]}}$ (°C)	$T_g^{\text{block 2 [e]}}$ (°C)
1	PBMgMes	10.0	10000	11900	1.06	-91	-
2	PB- <i>b</i> -EBR	21.6	21600	23800	1.13	-91	-33
3 ^[a]	PB- <i>b</i> -EBR	21.5	21500	24000	1.17	Nm	nm
4	PB- <i>b</i> -PE	16.4	16400	14200	1.43	-92	+124 ^[f]
5	PSMgMes	5.0	15000	14700	1.06	97	-
6a	PS- <i>b</i> -EBR	15.5	46500	44500	1.44	99	-33
6b ^[b]	Purified PS- <i>b</i> -EBR	-	46500	57100	1.27	99	-33

For B anionic polymerizations: $n\text{BuLi}$ = 1 mmol, 10 g of butadiene, 82 mL toluene, 53°C, 150 min. For CCT(co)P (runs 1-4): **1** = 240 μM for EBR and 60 μM for PE, PBMgMes = 3.33 mM, MesMgBr = 1.66 mM, 3.5 bars, E/B = 80/20, 300 mL toluene, 80°C. For S anionic polymerization: $n\text{BuLi}$ = 0.33 mmol, ETE/Li = 0.2, 5 g of S, 40 mL toluene, 40°C, 20 min. For CCT(co)P (runs 5-6): **1** = 250 μM , PSMgMes = 1.65 mM, MesMgBr = 1.35 mM, 3.5 bars, E/B = 80/20, 200 mL toluene, 90°C. [a] PBMgMes stored 30 days at -20 °C. [b] After removing PS fraction. [c] $M_n^{\text{theo}} = m_{\text{polymer}}/n(n\text{BuLi})$. [d] Determined by SEC in THF using universal calibration for polymers based on PB and conventional calibration using PS standards for polymers based on PS. Determined by HT-SEC in 1,2,4-trichlorobenzene for PB-*b*-PE. [e] Determined by DSC. [f] Melting transition temperature of PE block.

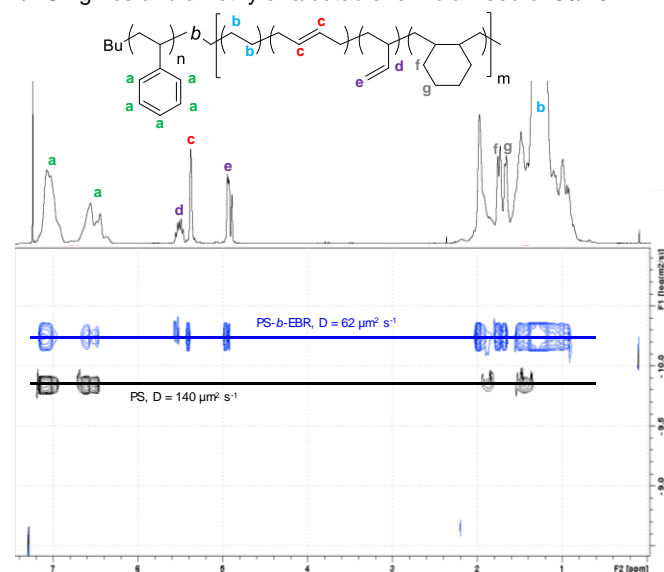
In the strategy employed by Fontanille et coll., the switch from anionic to catalytic coordination insertion polymerization was implemented by reacting PBLi with TiCl_4 .^[18] During the olefin coordination-insertion polymerization step, the resulting catalytic system was indeed able to insert the double bond from the 1,2 inserted B unit in PB chains leading to crosslinking reaction. In our system, the block copolymers were fully soluble and no crosslinking occurred during the catalytic process. Actually, the lack of reactivity of the neodymium catalyst toward α -olefin prevented the aforementioned side-insertion observed with Ti catalyst, which is a great advantage here for the production of block copolymers based on polybutadiene. In run 3 (Table 1), the macroCTA suspension employed was stored at -20°C for 30 days just after the transmetalation reaction. The results obtained after CCTcoP of ethylene and butadiene are similar (Figure S4) to the ones obtained for run 2 and showed the high stability under storage of PBMgMes.

**Figure 1.** SEC traces of PBMgMes and the formed diblock copolymer PB-*b*-EBR obtained after CCTcoP of E and B mediated by **1**/PBMgMes catalyst.

As **1** is also able to mediate the CCTP of E,^[37] the catalyst **1**/PBMgMes was also successfully used for the preparation of PB-

b-PE amorphous-crystalline block copolymers (Table 1, run 4 and Figures S5-S6). This polymer features a glass transition temperature of a soft PB block at -92°C and a melting transition at 124°C corresponding to the semi-crystalline PE block (Figure S7).

Targeting block copolymers from PS chains obtained by anionic polymerization is indeed challenging as the reinitiation was not successful when transfer onto Ti or V centers was implemented.^[18,21] A PS of 15000 g mol⁻¹ was prepared by anionic polymerization in toluene using $n\text{BuLi}$ as initiator and ethyl tetrahydrofurfuryl ether (ETE) as polar additive. PSLi was then reacted with an excess of MesMgBr to provide PSMgMes (M_n = 14700 g mol⁻¹, \bar{D} = 1.06) (Table 1, run 5). Considering the initiation of one EBR chain per introduced $n\text{BuLi}$, a PS-*b*-EBR with an EBR segment of 30000 g mol⁻¹ was targeted in a second step using **1**/PSMgMes and an ethylene/butadiene molar feed of 80/20.

**Figure 2.** DOSY NMR analyses of PS (Table 1, run 5, black trace) and the diblock copolymer PS-*b*-EBR (Table 1, run 6b, blue trace) performed in CDCl_3 at 25 °C.

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The SEC analysis agreed with the PS chain extension. It also shows the presence of dead PS chains (Figure S8) in the final product that could easily be discarded by selective precipitation in acetone (Table 1, run 6b). Purification by precipitation allowed to quantify gravimetrically the fraction of these PS chains to 10 wt%. After purification, a PS-*b*-EBR of 57100 g mol⁻¹ and a dispersity of 1.27 is isolated (Table 1, run 6b). ¹H NMR analysis shows the characteristic signals of both PS and EBR and a composition of 24% of PS and 76% of EBR is determined.

As expected, PS-*b*-EBR block copolymer features a soft EBR block with a $T_g = -33^\circ\text{C}$ and a hard PS block with a $T_g = 99^\circ\text{C}$ (Figure S9). In order to definitively confirm the formation of the targeted diblock copolymer, the starting PS chains and the purified PS-*b*-EBR were analyzed by Diffusion Ordered nuclear magnetic resonance Spectroscopy (DOSY NMR) (Figure 2 and Figures S10-S11).^[38] Analyses were performed in CDCl₃ at 25°C and a diffusion coefficient (*D*) of 140 μm² s⁻¹ is determined for PS. Only one diffusion trace is observed for the purified PS-*b*-EBR and the characteristic signals of both blocks fit with the same diffusion coefficient (*D* = 62 μm² s⁻¹). These results confirmed the formation of the targeted diblock copolymer.

The introduction of functional group at polymer chain-ends of apolar polymers like polydienes is of high interest since their properties can be improved.^[39] We have then investigated the preparation of end-functionalized block copolymers starting from end-functional PB. Hexamethyleneimide lithium can initiate the anionic polymerization of butadiene and equip the chains with an amine end-group.^[40,41] This functional group was selected due to his ability of interaction with inorganics and to bring properties of industrial interest.^[42] We thus further used lithium hexamethyleneimide (HMNLi) as initiator. It was obtained by reaction of one equivalent of *n*BuLi with hexamethyleneimine. In order to compare the data with *n*BuLi, anionic polymerization of B initiated by HMNLi (Table 2, run 7) was performed in similar conditions as run 1 (Table 1). HMNLi led to slightly broader PB molar mass distributions ($\bar{D} = 1.26$, Figure S12) than *n*BuLi ($\bar{D} = 1.06$), presumably due to a slower initiation rate. In order to improve initiation, polar additive such as ETE was used with

HMNLi and lower dispersity (1.12) was indeed achieved (Table 2, run 9 and Figure S13). The addition of ETE additionally influenced the microstructure (Table S1) and leads to an increase of 1,2-butadiene unit content in the chains. Consequently, higher glass transition temperature is observed (Table 2 and Figure S14). After transmetallation with MesMgBr, CCTcoP of E and B was successfully resumed in the presence of **1** and a nice shift of the molar mass distributions towards higher values were observed in all cases (Figures S12-S13). In a previous work we have investigated the addition of ether as cosolvent with similar catalyst systems and have shown an increase in activity for ethylene polymerization attributed to the coordination of ether to magnesium.^[37] In the present case, the same polymerization rates were observed in copolymerization of ethylene with butadiene in presence or absence of ETE. In addition, ETE does not impact the process and a molar mass distribution with dispersity of 1.21 for HMN-PB-*b*-EBR was obtained (Table 2, run 10). The synthesis of α-functional HMN-PB-*b*-EBR is confirmed by ¹H NMR analysis (Figure 3). Interestingly, no dead PB chains are observed when polymerizations were carried out in methylcyclohexane. PB dead chain observed in toluene might arise from chain transfer reaction with this solvent.^[43,44]

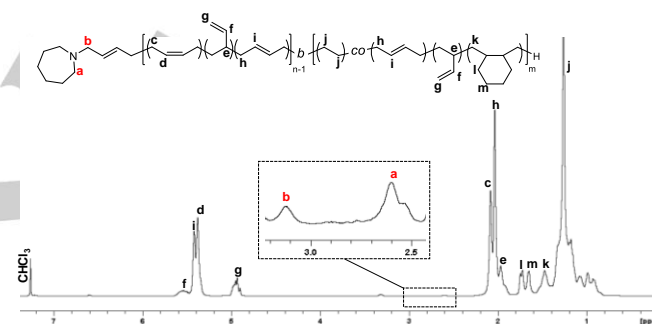


Figure 3. ¹H NMR spectrum of amino α-functionalized HMN-PB-*b*-EBR diblock copolymer (Table 2, run 8) in CDCl₃ at 25 °C.

Table 2. Polymerization data of polymers used and obtained for the targeting synthesis of functional HMN-PB-*b*-EBR or HMN-SBR-*b*-EBR diblock copolymers.

Run	Polymer	Yield (g)	M_n^{theo} [b] (g mol ⁻¹)	M_n^{SEC} [c] (g mol ⁻¹)	\bar{D} [c]	$T_g^{\text{block 1}}$ [d] (°C)	$T_g^{\text{block 2}}$ [d] (°C)
7	HMN-PBMgMes	8.8	10100	10000	1.26	-91	-
8	HMN-PB- <i>b</i> -EBR	21.2	24400	21900	1.26	-89	-34
9 ^[a]	HMN-PBMgMes	9.3	10700	9800	1.12	-65	-
10	HMN-PB- <i>b</i> -EBR	21.3	24500	21700	1.21	-64	-34
11 ^[a]	HMN-SBRMgMes	10.0	11500	10700	1.23	-45	-
12	HMN-SBR- <i>b</i> -EBR	21.4	24600	22300	1.24	-46	-32

For B anionic polymerizations: HMNLi = 0.87 mmol, ≈ 9 g of butadiene, 92 mL methylcyclohexane, 53°C, 60 min (120 min for run 8). For S/B anionic polymerizations: HMNLi = 0.87 mmol, ≈ 10 g of butadiene and styrene (butadiene/styrene = 75/25 wt/wt), 92 mL methylcyclohexane, 53°C, 60 min. For CCT(co)P: **1** = 240 μM, PMgMes = 2.9 mM (P: PB or SBR), MesMgBr = 2.1 mM, 3.5 bar, E/B = 80/20, 300 mL methylcyclohexane, 80°C. [a] 0.07 mmol of ETE. [b] $M_n^{\text{theo}} = m_{\text{polymer}}/h(\text{HMNLi})$. [c] Determined by SEC in THF using universal calibration. [d] Determined by DSC.

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In the objective to further modulate the properties of the block copolymers produced using our strategy, HMNLi was used to polymerize a feed of styrene and butadiene in order to form HMN-SBRMgMes after transmetallation. ETE was again used as polar agents. An efficient initiation is observed as shown by the good agreement between experimental and theoretical M_n (Table 2, run 11 and Figure S15).

The formation of HMN-SBR-*b*-EBR block copolymers is successful and confirmed by the shift of the molar mass distribution towards higher values and the obtained low dispersity of 1.24 (Table 2, run 12 and Figure S15).

Conclusion

Block copolymers were prepared for the first time by successive anionic and coordinative chain transfer polymerization. Our unique strategy is based on the preparation of macroCTAs formed by anionic polymerization and after transmetallation using MesMgBr performed directly into the anionic polymerization media. These macroCTAs are successfully involved without further purification in CCTP of olefins. PB-*b*-EBR and SBR-*b*-EBR copolymers with two soft block and possibly an amine chain-ends were obtained. In addition, soft and hard blocks can be combined in PS-*b*-EBR and PB-*b*-PE copolymers. This robust strategy enables to prepare block copolymers in a catalytic way and to produce a vast range of materials under simple and industrially viable conditions. The investigations of the mechanical properties of these copolymers are in progress and will be published in future works.

Acknowledgements

The authors thank the Manufacture Française des Pneumatiques Michelin for support. They thank the NMR Polymer Center of Institut de Chimie de Lyon for access to the NMR facilities and Fernande Da Cruz-Boisson (IMP/UMR5223) for assistance and fruitful discussion for the DOSY analyses.

Keywords: anionic polymerization • CCTP • metallocene • block copolymers • polyolefins

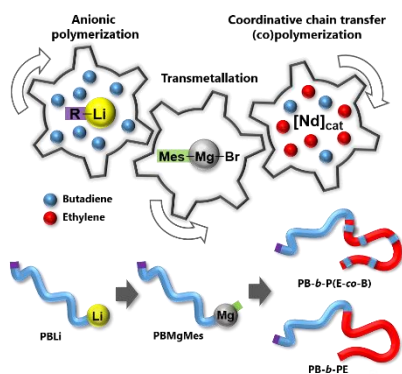
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Successive anionic polymerization and transmetalation reaction were used to design in situ macromolecular chain transfer agents involved in coordinative chain transfer copolymerization (CCTcoP) of ethylene and butadiene. Olefin block copolymers were formed for the first time by the switch from anionic polymerization to CCT(co)P.