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Efficient One-pot Synthesis of End-functionalized *trans*-stereoregular Polydiene Macromonomers

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ABSTRACT. End-functionalized 1,4-*trans*-polydienes (isoprene, myrcene) were prepared by means of a neodymium mediated continuous polymerization-functionalization process. A chain transfer stage was essential to get a high level of functionalization of the polymer. The living 1,4-*trans* stereoregular polymer chain was reacted with benzophenone to afford up to 97 % -CPh_2OH end-group with isoprene, while in the case of myrcene, using the same strategy afforded 1,4-*trans* polymyrcene with a functionalization rate of 83 %. The strategy was validated with complementary functionalization experiments using benzaldehyde and styrene oxide, both affording 95 % end-capped *trans*-stereoregular polydienes.

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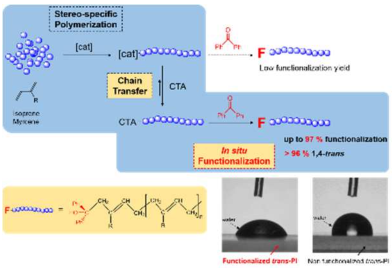
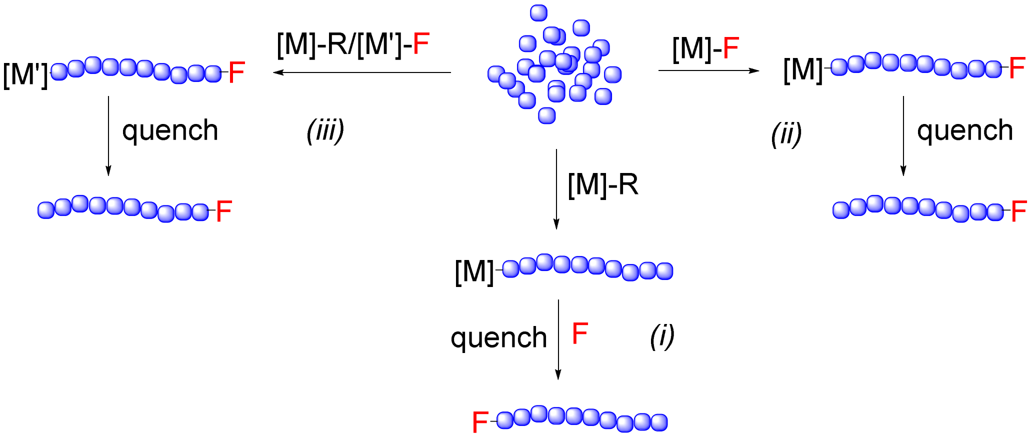


INTRODUCTION

The synthesis of polyolefins having a defined microstructure and incorporating functional polar groups at the chain-end(s) is one of the major challenges of polymer science.[1] This offers unique features regarding physical-chemical properties like adhesion, paintability, miscibility/compatibility in blends and also in terms of chemical reactivity with the possibility to use these macromolecular objects as reactive building blocks, in order to further access to *hybrid* polymers with sophisticated architectures.[2,3] One seducing synthetic approach in that frame, which is in principle authorized by living polymerization as recalled by Coates *et al.*,[4] is the achievement of the end-functionalization in the *continuum* of the polymer chain growth. By comparison, the more tedious post-functionalization, which is part of a multi-step chemistry transformation, requires a prior isolation of the polymer. Up to now, important breakthroughs in terms of end-functionalized polymers have been obtained with ethylene and α-olefins, thanks to the living character offered by Coordinative Chain Transfer Polymerization (CCTP).[5-11] On the other hand, the preparation of polydienes bearing polar end-groups can be obtained by anionic polymerization of conjugated dienes, however, this strategy is limited to non-stereo-regular polymers.[12,13] As far as stereospecific polymerization of conjugated dienes is concerned, and apart from block copolymers issued from a sequenced feed of non-polar monomer followed by addition of polar monomers,[14-18] the elaboration of stereoregular polydienes that are also *quantitatively* end-functionalized remains a challenge that, to date, has scarcely been attained.[19-25] Several pathways can *a priori* be envisioned to achieve this goal of preparing end-functionalized stereo-regular polydienes (Scheme 1). The simplest way is to insert (*i*) a small electrophilic molecule, after full conversion of the monomer, into the living metal catalyst-macromolecular chain bond. More time-consuming pathways are to use a stereo-specific catalyst (*ii*) comprising a functionalized initiating group, or (*iii*) combined with a CTA that bears a functional group (CTA for Chain Transfer Agent, in excess). A main drawback of the approaches *(ii)* and *(iii)* is that they require the prior preparation of a rather sophisticated functionalized catalyst or CTA molecules.[25,26] Therefore, focusing on more straightforward approaches such as (*i*) are highly desirable. Despite interesting results found in the patent literature[19-24] and the mention of *cis*-polyisoprene bearing one terminal carboxylic functionality − where quantification details of the functionalization are lacking −,[27] a general strategy that would allow the easy preparation of stereoregular polydienes having high level (> 90 %) of end-functionalization has not been reported to our knowledge.



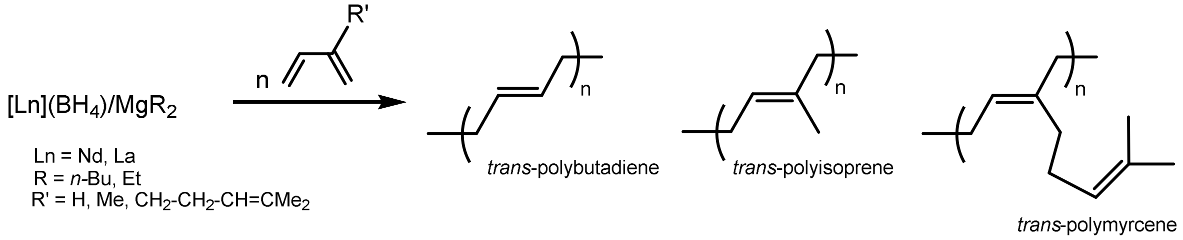
Scheme 1. The three proposed pathways to synthesize end-functionalized stereo-regular polydienes (M = metal catalyst, M' = main-group metal CTA, ● = motive of stereo-regular polymer chain, F = functional group).

Our group has significantly contributed to the *trans*-polymerization of conjugated dienes by means of dual rare earths/dialkylmagnesium catalysts,[28-30] and we therefore selected such catalysts to target the preparation of end-functionalized *trans*-regular polydienes. *Trans*-polyisoprene is a material that displays good dynamic mechanical properties, which makes it a good candidate as a co-component for high-performance tires.[31,32] *Trans*-regular polydienes that would bear a polar end-group may thus be of high interest for blending with inorganic loadings like silica. On the other hand, the opportunity to include a *trans*-polydiene sequence in a macromolecular object can lead to polymer materials offering a new range of mechanical properties.[1] From a more fundamental point of view, the possibility of adding a functional group at the extremity of a macromolecular chain in the *continuum* of a stereoselective conjugated diene polymerization process would also be a proof of livingness, as highlighted in 2006 in the review of Friebe *et al.*.[33] As described in the recent study of Mecking, direct quenching of the *trans*-polymerization of isoprene failed to afford more than 50 % functionalization rate.[25]

Typically, the strategy implemented in this work consists of a simple addition of an electrophilic organic molecule to a reaction mixture containing a living stereoregular polymer, subsequently to the polymerization process, but moreover taking advantage of the reversible transfer of the living chains prior to the quench of the reaction. A comparison of different stereoregular dienes end-functionalization approaches will be also proposed in the present study. Our strategy enabled us to achieve one-pot syntheses of polydienes combining more than 95 % *trans*-stereoregularity and a terminal alcohol functionality with rates up to 97%.

RESULTS AND DISCUSSION

1,4-*trans*-stereoregular (up to 98%) polydienes are accessible via borohydrido lanthanide/dialkyl magnesium mediated polymerization as recently described in our group (Scheme 2).[29]



Scheme 2. 1,4-*trans*-selective polymerization of conjugated dienes with Ln[BH_4]/MgR_2 catalysts

In order to achieve the *in situ* functionalization of these polymer materials, we envisaged three different approaches, by addition of an electrophilic molecule, once the monomer conversion –

by means of the dual [Ln(BH_4)]/BEM catalyst (Ln = lanthanide, BEM = *n*-BuEtMg) – was considered as being completed:

(1) directly to the polymerization reaction mixture,

(2) to the reaction mixture under CCTP conditions (*i.e.* with BEM/AlR_3 in excess as cocatalyst or CTA),

(3) to the reaction mixture but posterior to the reaction with BEM or *n*-BuLi in excess.

Benzophenone was chosen as the electrophilic substrate model to afford functionalized polydienes because of its ability to be cleanly inserted into a lanthanide-allyl moiety.[34,35] Low monomer to catalyst ratios were intentionally chosen, in order to be able to measure more accurately the rate of terminal functionalization. Selected results are gathered in Table 1.

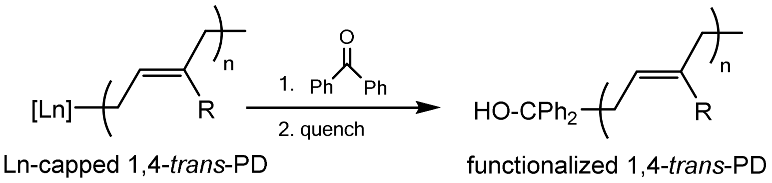
Table 1. *In situ* stereoselective polymerization-functionalization of conjugated dienes

Run[a]	**Monomer (equiv)**	**CTA (equiv)**	**Polymer Yield (%)**	***M*n (Đ)**[b]	**Microstructure (%)**[c] **1,4- (*trans/cis*)**	**3,4-**	**F (%)**[c]
1	Isoprene (200)	-	80	6000 (1.8)	98.8 (50/1)	1.2	49
2	Myrcene (200)	-	82	22300 (1.7)	98.8 (40/1)	1.2	65
3[d]	Isoprene (1000)	BEM (1) / $AlEt_3$ (9)	79	3900 (2.5)	98.4 (8/1)	1.6	81
4[e]	Myrcene (200)	BEM (1) / Al(*i*-Bu)$_3$ (19)	95	11600 (2.7)	97.5	2.5	> 85
5	Isoprene (200)	BEM (10)	76	5300 (1.6)	98.6 (40/1)	1.4	89
6	Myrcene (200)	BEM (10)	89	26600 (1.6)	99.2 (45/1)	0.8	72
7	Isoprene (200)	*n*-BuLi (20)	>99	3800 (1.3)	97.4 (44/1)	2.6	92

7’	Isoprene (50)	*n*-BuLi (20)	>99	1000 [f]	96.7	3.3	97
8	Myrcene (200)	*n*-BuLi (20)	76	18800 (1.5)	98.0	2.0	83

[a] First stage: pre-catalyst = $Nd(BH_4)_3(THF)_3$ (17 µmol), [BEM] / [Nd] = 1, V(monomer) = V(toluene), t = 2 h , T = 50 °C ; intermediate stage of reaction with a Chain Transfer Agent (CTA, 50 °C, 1 h); last stage: [benzophenone] / [CTA alkyl group] = 2, t = 12 h, T = 50 °C. [b] Determined by SEC by reference to PS standards and (i) corrected by a factor of 0.5 for 1,4-*trans*-polyisoprene,[36] (ii) not corrected for 1,4-*trans*-polymyrcene.[37] [c] Determined by ^1H NMR. [d] Nd 10 µmol, polymerization time: t = 24 h. [e] Nd 10 µmol, polymerization time: t = 72 h. [f] SEC not performed, M_n value was deduced from ^1H NMR by relative integration of the terminal methyl (δ = 0.8 ppm) and skeleton $-CH_2CH_2-$ (δ = 1.9 ppm) signals.

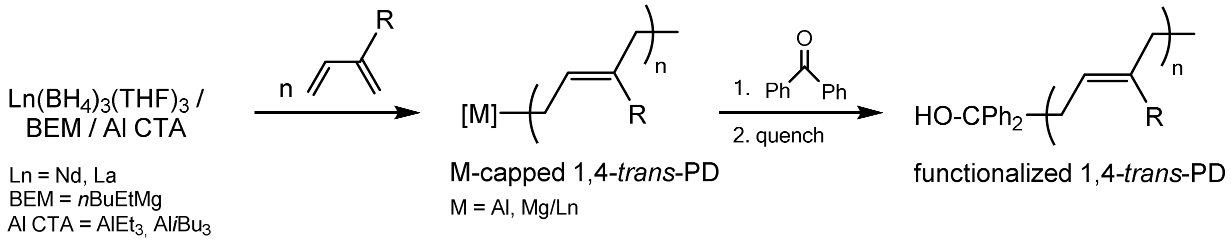
The first attempts were conducted by direct reaction of benzophenone in excess with a – putatively – living 1,4-*trans*-polyisoprenyl chain grown with the $Nd(BH_4)_3(THF)_3$/BEM catalytic system (runs 1,2), according to Scheme 3. A similar procedure was followed by Cramail *et al.* in the case of anionic non-stereoselective polymerization of isoprene.[38]



Scheme 3. Direct *in situ* reaction of the catalyst-capped macromolecular chain with benzophenone (PD polydiene, PD = PI, R = Me; PD = PMy, R = $CH_2CH_2CH=CMe_2$, PI polyisoprene, PMy polymyrcene; Ln = Nd, La).

As a result, only partially functionalized 1,4-*trans*-polyisoprene (Table 1) was isolated: whatever the experimental conditions, the functionalization (determined by ^1H NMR integration, deduced from the relative *Me*/C*Ph*$_2$ end-groups integration, see a typical example further in Fig. 1) was invariably limited to less than 50 % (run 1, Fig. S1, SI section). With myrcene and under similar experimental conditions, 1,4-*trans*-polymyrcene having up to 65 % functionalized end-group was recovered (run 2, Fig. S2, SI section). These results confirm those obtained by Mecking,[25] and may be related to the nature of the propagating species in the course of the polymerization: it is generally accepted that [Ln/Mg] bimetallic entities are formed in such media, and particularly when bridging BH_4 moieties are present in the coordination sphere of the catalyst.[39,40] Therefore, the reactivity of the (dual metal) catalyst-polydienyl chain may no longer be that of a simple lanthanide-allyl moiety.[38,41,42] Moreover, it must be reminded that the reactivity of rare-earth metal allyl may also subtly depend on the nature of the metal: La-allyl easily inserts Ph_2CO while Y-allyl is inert towards the same reaction.[34] We also noted that the dispersity remained fairly narrow for both runs 1 and 2 (1.7), while the experimental M_n values after correction match quite well with the theoretical ones. These results are similar to the ones reported for non-functionalized polydienes obtained with this catalyst, and allow to consider that the functionalization step does not disturb the *quasi*-livingness of the polymerization process.[29,43]

An alternative approach to synthesize $-CPh_2OH$ end-capped polydienes was to take advantage of the polymerization conditions in which CCTP (Coordinative Chain Transfer Polymerization), an area in which we have heavily invested since the 1990s,[44,46] is operating. The stage of the reaction with benzophenone was, as described in the previous case, conducted just after the polymerization reaction (Scheme 4). In this case, two different steps must be considered for the production of the functionalized polymer, since propagation and reversible transfer take place concomitantly during the polymerization.

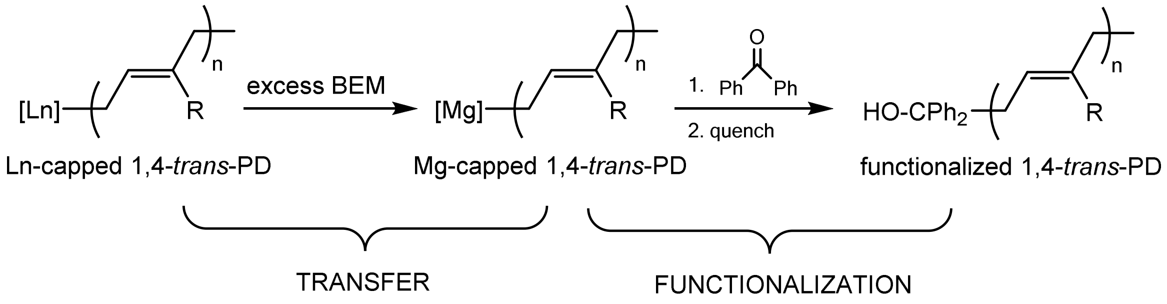


Scheme 4. Strategy of functionalization of a living 1,4-*trans*-polydiene macromolecule by benzophenone after CCTP reaction with lanthanide/magnesium catalyst in the presence of an aluminum chain transfer agent (PD = PI, R = Me; PD = PMy, R = $CH_2CH_2CH=CMe_2$; Ln = Nd, La).

The ternary Ln/Mg/Al catalytic combination was selected due to its ability to ensure *trans*-selectivity along with fair transfer efficiency in conjugated diene polymerization, leading to low M_n molecular materials.[47,48] In presence of triethylaluminum as CTA (run 3), the functionalization rate was simply deduced from the *Me* end-group integration *vs.* the Ph_2 one in the ^{1}H NMR spectrum. To quantify the percentage of functionalization in the case of Al*i*-Bu_3 as CTA (run 4), we had to take into account the fact that *ca.* 20 % of Al-alkyl groups are being involved in the chain transfer.[47] As a consequence, for run 4, where 19 equiv. Al*i*-Bu_3 are used, *i.e.* 57 equiv. alkyl groups, 57 x 20 % = 11.4 polymer chains bear an *i*-Bu end-group, and 2 chains bear a Me end-group (from initial BEM alkylation), all having signals located at *ca.* δ = 0.8 ppm. Since one *i*-Bu end-group integrates for 6 H, the integration of the Me resonance on which is based the calculation counts for [11.4 x 6 H (*Al*) + 2 x 3 H (*Mg*)]/ (11.4 + 2) = 5.5 H. This two-step procedure, which requires 24 h - 72 h reaction time, afforded finally 1,4-*trans*-polyisoprene (run 3, Fig. S3, SI section) and 1,4-*trans*-polymyrcene (run 4, Fig. S4, SI section) functionalized at 81 % and *ca.* 85 %, respectively. This improvement in the functionalization rate, when compared with the direct method, was in agreement with the well-known reactivity of an Al-allyl moiety towards the insertion of electrophilic substrates.[49,50]

Regarding the macromolecular data (M_n, Đ) obtained after that functionalization stage, they were unchanged, as expected, with respect to a standard *trans*-CCTP of isoprene (rather broad dispersity is generally observed when using the ternary Ln/Mg/Al catalytic combination under CCTP conditions [47,48]).

In order to improve this functionalization rate, we intended to study the influence of a large excess of magnesium dialkyl in the reaction mixture prior to the reaction with benzophenone. This idea was based on the known propensity of a polyisoprenyl chain to reversibly transfer from a lanthanide metal to magnesium, in the course of the polymerization process, as we demonstrated previously.[47] However, since it was also shown in the same study that a polymerization carried out in the presence of an excess of magnesium dialkyl leads to a loss of *trans*-stereoregularity, we added this excess of magnesium reagent in a second time only, with the aim to promote lanthanide to magnesium transfer of *trans*-stereoregular macromolecules, once the monomer conversion was completed. This strategy is represented on Scheme 5.



Scheme 5. Strategy of functionalization of a living 1,4-*trans*-polydiene macromolecule by *in situ* reaction with benzophenone posterior to transfer of the macromolecular chain from the Ln catalyst to a magnesium atom *via* addition of an excess BEM (PD = PI, R = Me; PD = PMy, R = $CH_2CH_2CH=CMe_2$; Ln = Nd, La).

The results related to this functionalization approach are given in Table 1 (runs 5, 6). We isolated after work-up 1,4-*trans*-regular polyisoprene that was bearing the expected diphenylhydroxymethylene end-group with a rate of 89 % (run 5, Figure 1). We observed that the prolonged reaction time of the final stage (one night, rather than 1 h reaction) at 50 °C was not efficient to improve the functionalization rate. This result, based on the reactivity of magnesium-polyisoprenyl with benzophenone, was in line with the expected reactivity of a magnesium-allyl moiety with an aromatic ketone.[51,52] Thankfully, macromolecular data (narrow dispersity 1.2-1.8) as well as stereoselectivity (> 97% 1,4-*trans*) were not altered by the two additional steps of transfer and functionalization, they were similar to a standard polymerization carried out with a dual Ln/Mg catalyst.[43] Therefore, the post-transfer reactions appear to be highly efficient, in addition to not disturbing the quasi-living character of the polymerization. In the case of myrcene under similar experimental conditions, the enhancement of the functionalization was less important than for isoprene, giving 1,4 *trans*-polymyrcene having a functionalization rate 72 % (run 6, Fig. S5, SI section).

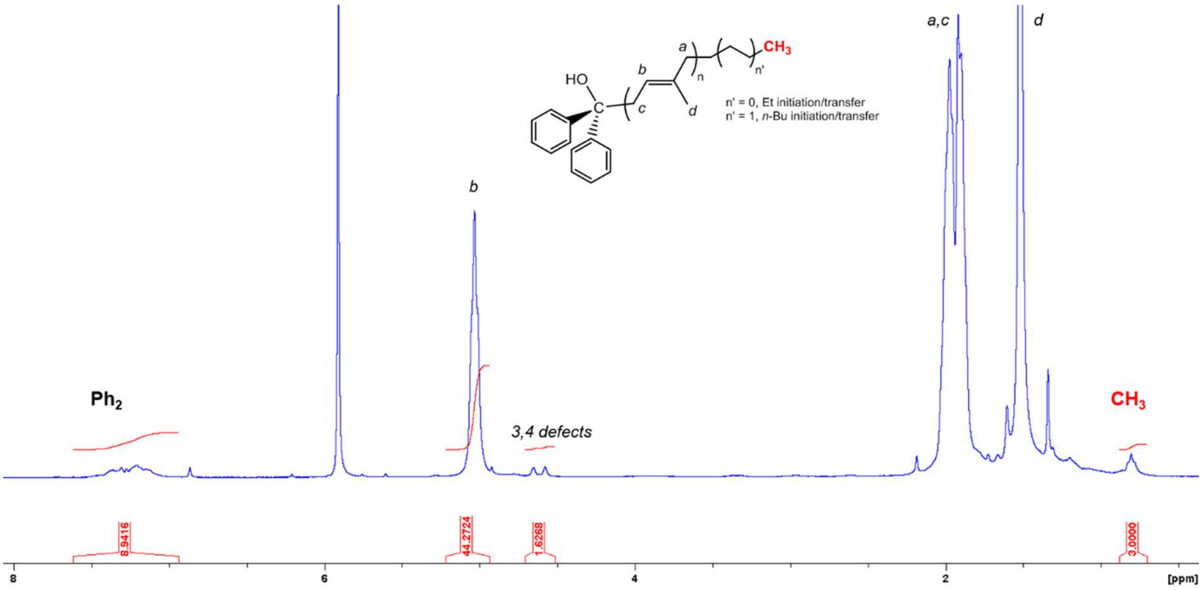
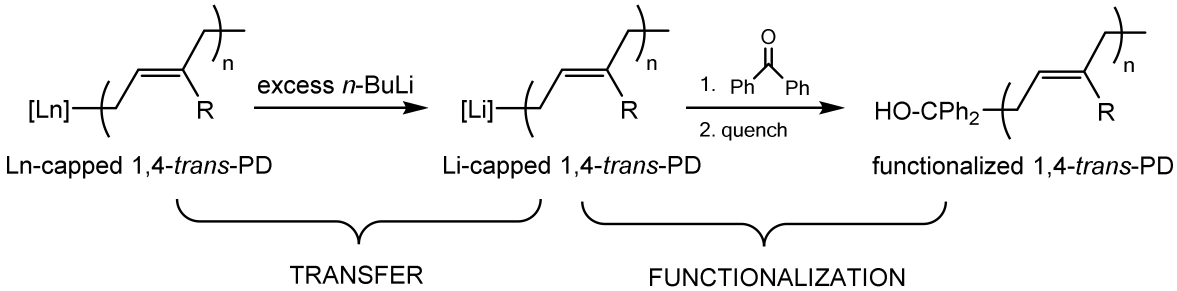


Figure 1. ^{1}H NMR spectrum of hydroxydiphenylmethylenyl-1,4-*trans*-polyisoprene (run 5, $C_2D_2Cl_4$, solvent residue at 5.91 ppm)

The macromolecular chain transfer (that can also be seen as transmetallation) step was then tentatively carried out with *n*-BuLi instead of BEM. This was considered as, on one hand, *n*-

BuLi can be used as transfer agent in combination with lanthanide catalysts in coordination polymerization[53-55] and, on the other hand, the reactivity of Li-polyisoprenyl with benzophenone to afford the functionalized polymer had been previously established.[38] As before, an excess (10 fold per initiating alkyl group) of lithium reagent was added after the polymerization was completed, in order to promote lanthanide to lithium transfer of the *trans*-stereoregular chains, and before the reaction with the electrophilic reagent (Scheme 6). According to ^{1}H NMR analysis, this method afforded higher percentage of functionalization when compared to the one involving transfer to Mg: 92 % (run 7) and 83 % (run 8) for isoprene and myrcene, respectively (Figs. 2 and 3). Coupling reactions known to occasionally occur with Mg-R species via radical process may explain the higher rate obtained with this *n*-BuLi strategy rather than with the BEM.[56] In the ^{1}H spectrum, as in the previous ones, there is no clear resonance that could be attributed to the expected OH signal. We propose that this is connected with the self-assembly behavior of the end-functionalized polyisoprene in solution as already observed by Cramail.[38] Finally, like in the case of the addition of BEM in excess, molecular weights and dispersity of the polymers are consistent with a typical *trans*-polymerization with the Ln/Mg dual catalyst without the final functionalization step.



Scheme 6. Strategy of functionalization of a living 1,4-*trans*-polydiene macromolecule by *in situ* reaction with benzophenone posterior to transfer of the macromolecular chain from the Ln catalyst to a lithium atom *via* addition of excess *n*-BuLi (PD = PI, R = Me; PD = PMy, R = $CH_2CH_2CH{=}CMe_2$; Ln = Nd, La).

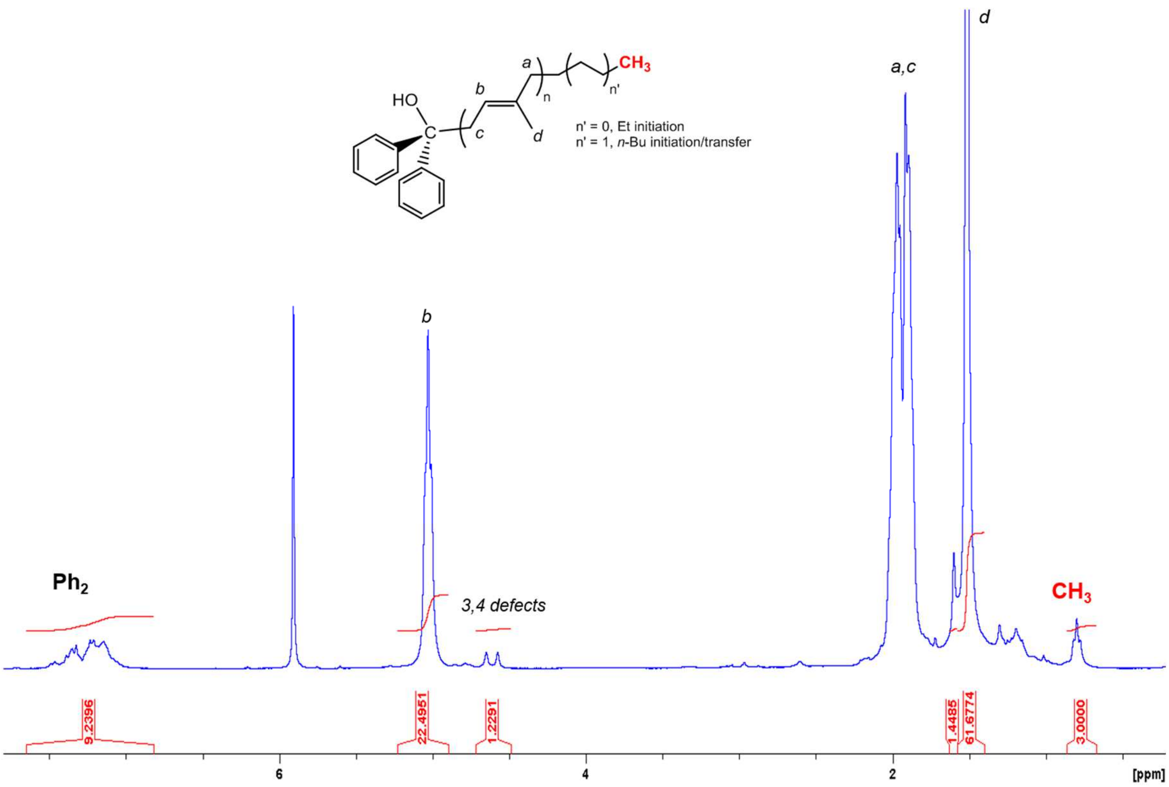


Figure 2. ^{1}H NMR spectrum of hydroxydiphenylmethylenyl-1,4-*trans*-polyisoprene (run 7, $C_2D_2Cl_4$, solvent residue at 5.91 ppm)

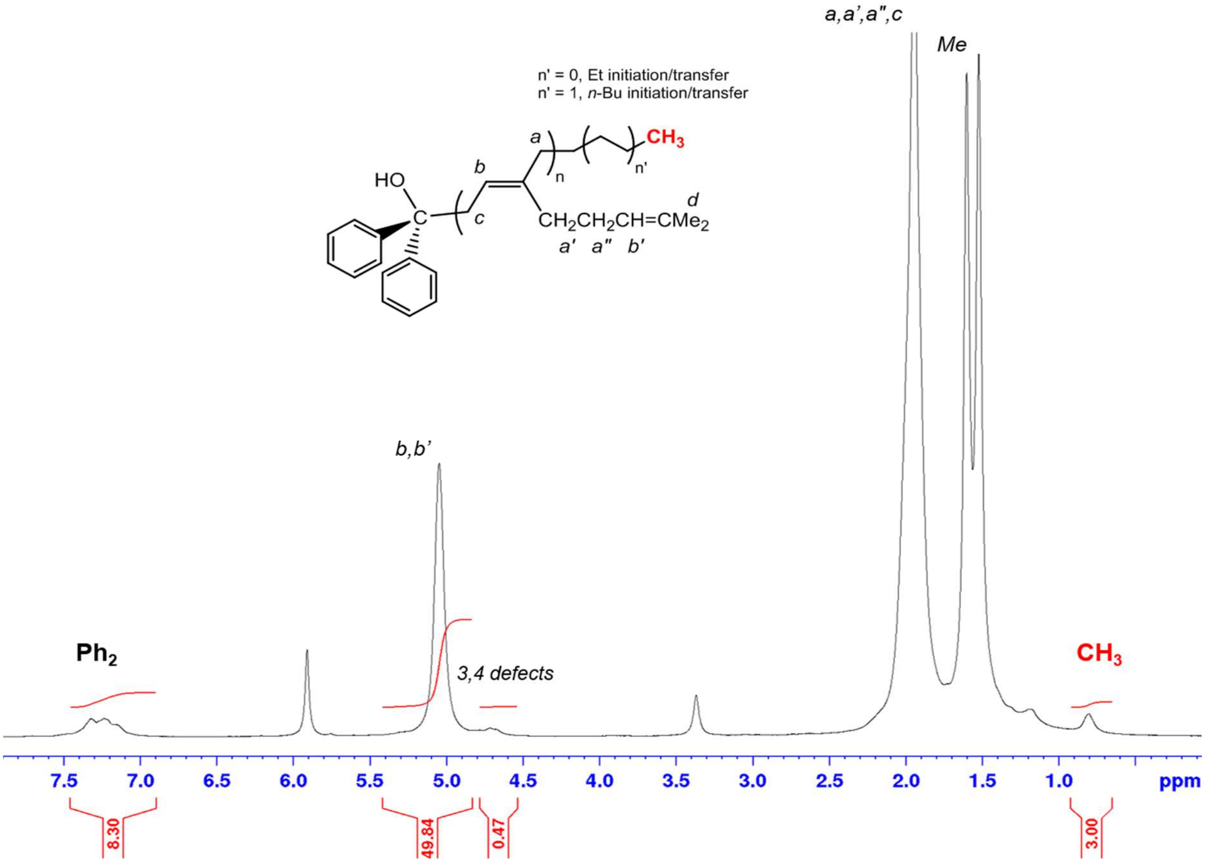


Figure 3. ^{1}H NMR spectrum of hydroxydiphenylmethylenyl-1,4-*trans*-polymyrcene (run 8, $C_2D_2Cl_4$, solvent residue at 5.91 ppm)

To facilitate the detection by ^{13}C NMR of the primary and tertiary sp^3 resonances expected for a terminal =C-***C***H$_2$-***C***Ph$_2$-OH group resulting from benzophenone insertion into a lanthanide-allyl moiety, we have prepared a low M_n 1,4-*trans*-polyisoprene sample using [isoprene]/[catalyst] ratio equal to 50 (run 7', other experimental conditions identical as run 7).[36] The ^{13}C JMod NMR spectrum of the oligomer isolated showed the typical resonances due to end-group status (Fig. S6, see SI section). By ^{1}H NMR analysis (Fig. S7, SI section) a functionalization rate of 97 % was found. DOSY NMR analysis was also performed on that polymer isolated from run 7', which definitely established the attachment of the CPh$_2$ moiety to the polydiene skeleton (Fig. 4), and therefore the effective functionalization of the 1,4-*trans*-stereoregular polydiene chains.

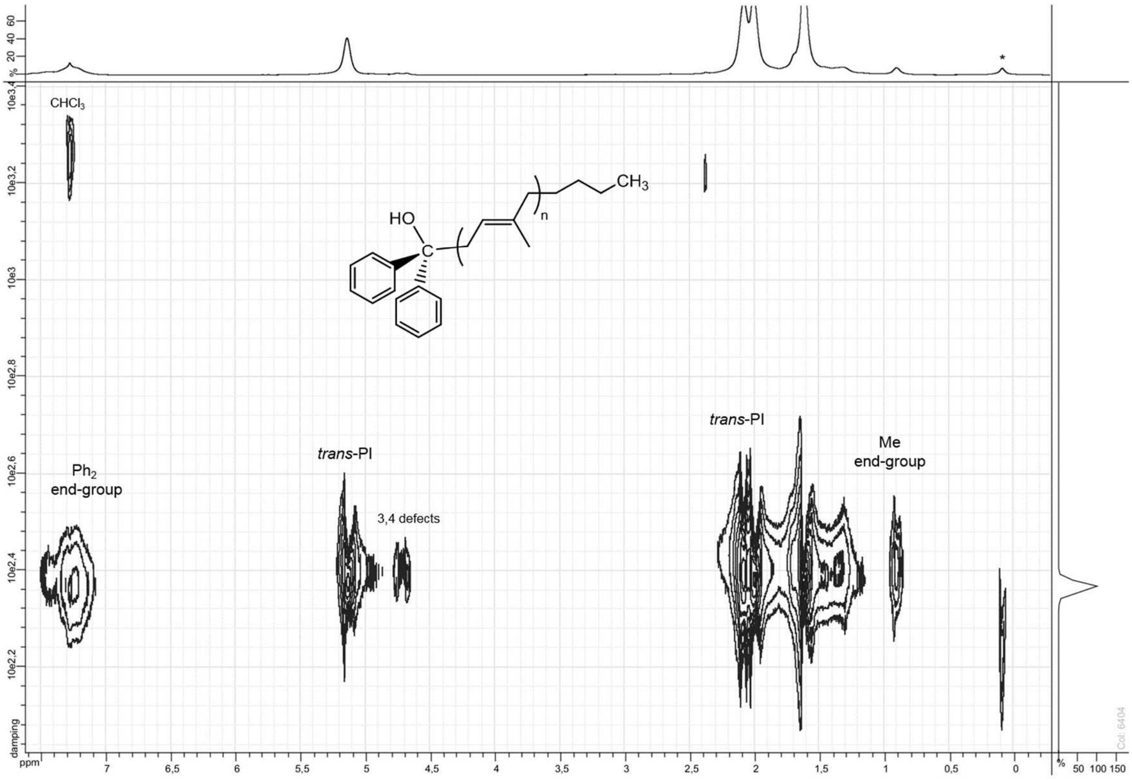


Figure 4. ^{1}H DOSY NMR spectrum of hydroxydiphenylmethylenyl-1,4-*trans*-polyisoprene (run 7', $CDCl_3$, * silicone grease impurity).

The IR spectrum of the polymer material isolated from run 7' is shown in Fig. 5, with reference to that of a standard non-functionalized 1,4-*trans*-polyisoprene [57] (abbreviated as TPI) synthesized as reported.[43] The absorbance at *ca.* 3300 cm^{-1} can be attributed to the hydroxyl end-group moiety, and its very broad character argues well for self-assembly of the polymer *via* hydrogen (OH) bonds, as postulated above.

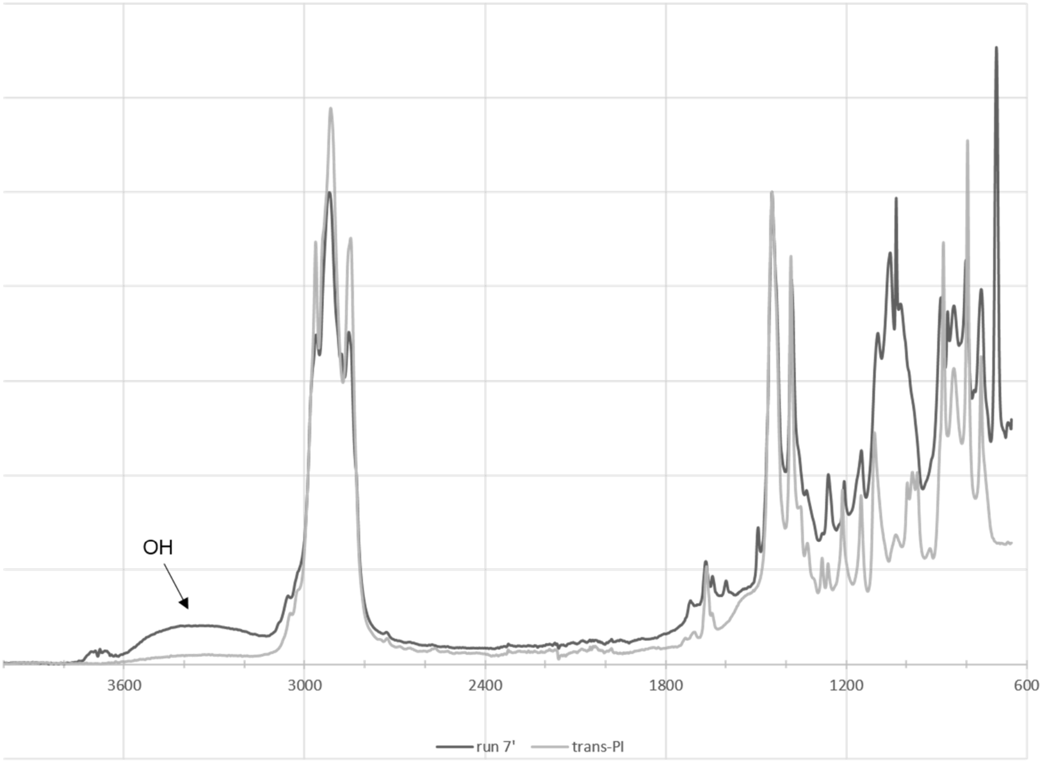


Figure 5. IR spectrum of functionalized 1,4-*trans*-polyisoprene received from run 7' (black line) and of non-functionalized 1,4-*trans*-polyisoprene (grey line).

We were able to confirm the increase of the polar character of a functionalized 1,4-*trans*-polyisoprene with respect to the same standard non-functionalized TPI: as shown in Fig. 6, drop angle measurements using water as reference liquid gave a mean value of 62.1 ° and 94.3 ° for classical and end-functionalized 1,4-*trans*-polyisoprenes, respectively.

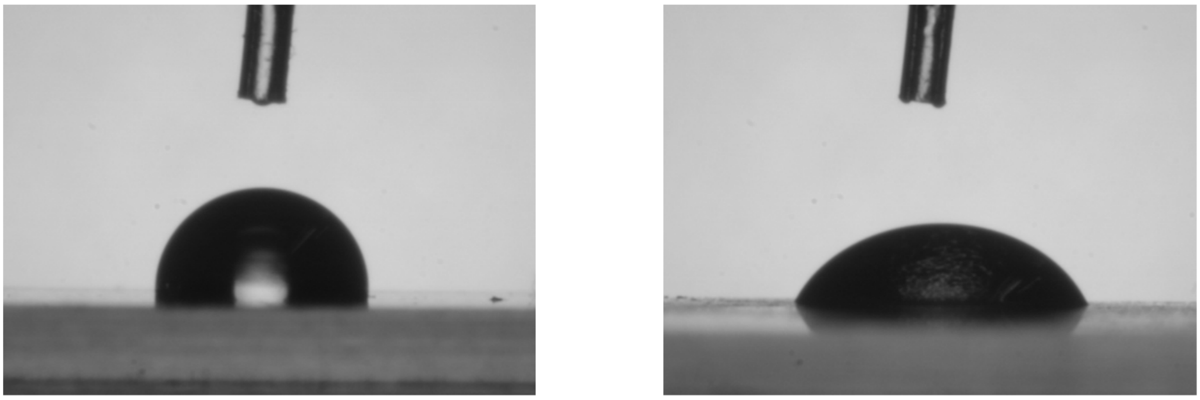
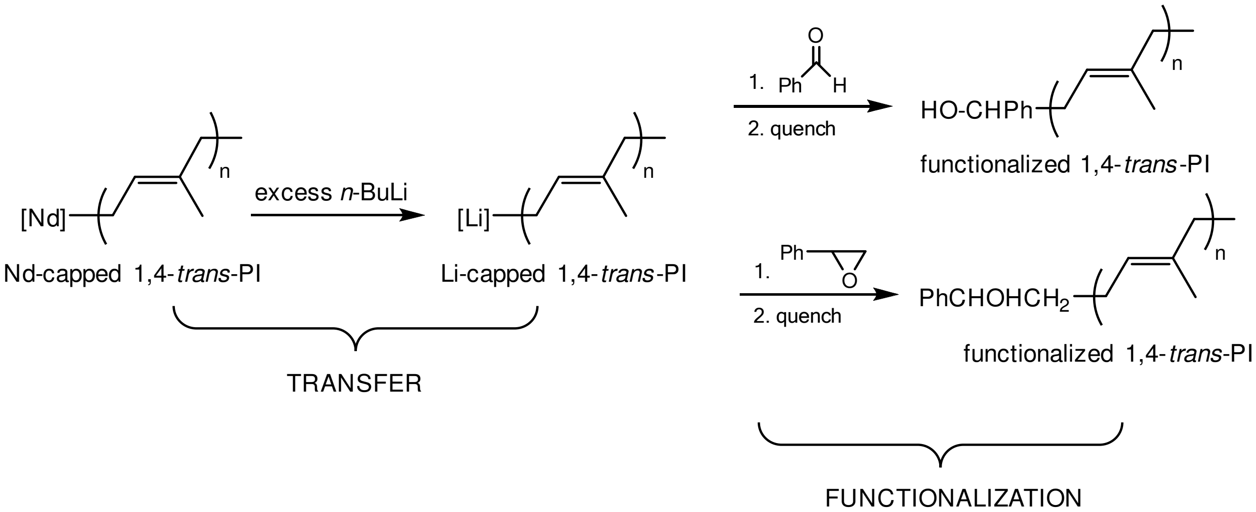


Figure 6. Pictures showing a drop of water placed on a film of 1,4-*trans*-polyisoprene (left) and of functionalized 1,4-*trans*-polyisoprene received from run 7' (right).

The success of the three-step polymerization/transfer/functionalization strategy described in this study (Schemes 5 and 6) was finally further confirmed by extending it to the reaction of a living *trans*-polyisoprenyl moiety with two other substrates: benzaldehyde and styrene oxide, as illustrated in Scheme 7. The results are presented in Table 2.



Scheme 7. Strategy of functionalization of a living 1,4-*trans*-polyisoprene macromolecule by *in situ* reaction with (top) benzaldehyde or (bottom) styrene oxide – assuming a major 1,2 nucleophilic addition – posterior to transfer of the macromolecular chain from the Nd catalyst to a lithium atom *via* addition of excess *n*-BuLi.

Table 2. ***In situ*** **stereoselective polymerization-functionalization of conjugated dienes**

Run[a]	**Monomer (equiv)**	**CTA (equiv)**	**Functionalization reagent**	**Polymer Yield (%)**	M_n **(Đ)**[b]	**Microstructure (%)**[c]		**F (%)**[c]
						1,4- (*trans/cis*)	**3,4-**	
9	Isoprene (200)	*n*-BuLi (20)	Benzaldehyde	>99	5900 (1.3)	98.0	2.0	95
10	Isoprene (200)	*n*-BuLi (20)	Styrene oxide	>98	5100 (1.3)	98.0	2.0	96

[a] First stage: pre-catalyst = $Nd(BH_4)_3(THF)_3$ (50 μmol), [BEM] / [Nd] = 1, V(monomer) = V(toluene), t = 2 h , T = 50 °C ; intermediate stage of reaction with a Chain Transfer Agent (CTA, 50 °C, 1 h); last stage: [functional reagent] / [CTA alkyl group] = 1, t = 16 h, T = 50 °C. [b] Determined by SEC by reference to PS standards and corrected by a factor of 0.5 for 1,4-*trans*-polyisoprene.[36] [c] Determined by ^{1}H NMR.

These additional experiments both resulted in the formation of *trans*-polyisoprenes having a high percentage of end-functionalization: 95% with benzaldehyde and 96% with styrene oxide on the basis of ^{1}H and ^{1}H DOSY NMR (see SI section Figs. S9-S14). In both cases the ^{1}H DOSY NMR established the grafting of the functional group at the extremity of the polymer chain.

CONCLUSION

To summarize, we present two strategies in this study that allow the preparation of end-functionalized 1,4-*trans*-stereoregular polydienes and differ on a number of points:

- a two-step (CCTP-functionalization) strategy: under CCTP conditions, polymerization is followed by functionalization, and chain transfer takes place concomitantly to the propagation. The polymerization time is rather long, low to medium M_n values can be obtained, and excess Al co-catalyst is required;

- a three-step (polymerization-transfer-functionalization) strategy: both approaches with BEM and *n*-BuLi as post-CTA include an additional stage to complete the polyisoprene chain transfer from the metal catalyst. Although a three-step procedure, the total reaction time is shorter, but it can afford higher M_n values. A 20-fold excess of alkylating reagent per alkyl is used in those cases.

The second approach allowed the isolation of *trans*-polyisoprene up to 97 % end-functionalized. It could be successfully extended to other substrates like benzaldehyde and styrene oxide, to give a similar amount (ca. 95%) of functionalization, which validates the concept.

These strategies advantageously compare with the direct addition of a small molecule in the reaction mixture containing the potentially reactive "living" macromonomer, which is known to stay limited to a low percentage (< 65 %) of functionalization.

Finally, the high yield of functionalization obtained definitely establishes the quasi-living character of the conjugated dienes polymerization with the $[Ln(BH_4)]MgR_2$ catalytic system, but it was necessary to clinch the polymer chain from the metal catalyst to confirm it. Further studies aiming to improve the process and varying the nature of the end-functionality, as well as studying the influence of the molecular weight to the functionalization, are in progress.

The strategies developed in this work pave the way for the development of new ranges of functional elastomeric materials in a next future.

EXPERIMENTAL SECTION

Materials and methods. All operations were performed under dry argon using a glove box (Jacomex) or Schlenk techniques. Toluene was purified through an alumina column (Mbraun SPS), stored, trap-to-trap distilled over sodium/benzophenone, and stored on 4A molecular sieves in a glove box. Isoprene and Myrcene (Aldrich) were dried over calcium hydride, distilled once over 4A molecular sieves, and once again just before use. Metal alkyls (*n*-BuLi, 2.1 M in hexanes, Aldrich; *n*-BuMgEt or BEM, 20 wt% in heptane from Texas Alkyls; Al(*i*-Bu)$_3$ or TIBA, AlEt$_3$, Aldrich) were used as received. NMR (^{1}H, ^{13}C) spectra were recorded on a Bruker Avance 300 apparatus at room temperature in CDCl$_3$. The chemical shifts were calibrated using the residual resonances of the solvent. SEC analyses were performed in THF at 40 °C with a Waters apparatus, calibrated with polystyrene standards, equipped with Waters Styragel columns HR2, HR3, HR5 and HR5E. Drop angle measurements were performed with a Digidrop Contact Angle Meter (GBX Scientific Instruments). The software Windrop++ was used to determine the contact angle (mean value of 5 experiments) of a 10 µL drop of water placed on a glass surface covered with a film of polymer, which was prepared by evaporation of a toluene solution (50 mg polymer/1 mL toluene).

NMR experiments. One-dimensional NMR spectra (^{1}H, 400.33 MHz and ^{13}C, 100.66 MHz) were recorded on a Bruker avance II 400 Instrument (9.4 T) equipped with a TBI 5mm inverse z-gradient probe probe. All the experiments were recorded using C$_2$D$_2$Cl$_4$ as solvent. The solutions were transferred in 5 mm NMR tubes, giving a sample total volume of 600 µl. The probe temperature was regulated at 298 K. The chemical shifts were calibrated using the residual resonances of the solvent (δ = 5.91 ppm and 74.0 ppm for ^{1}H and ^{13}C respectively). Typical acquisition ^{1}H parameters consisted of 64K points covering a sweep width of 6000 Hz and 64 transients. No digital zero filling and a 0.3 Hz exponential function were applied to the FID before Fourier transformation. Typical experimental Jmod ^{13}C values include the following sweep width of 24000 Hz, 64K real acquisition points and 18688 transients. No digital zero filling and a 5 Hz exponential function were applied to the FID before Fourier transformation. The ^{1}H DOSY pulse program was ledbpgp2s. Typical acquisition parameters consisted of 8K points covering a sweep width of 4800 Hz. td1: number of experiments was 16 and number of scan was 128. We used NMR notebook copyright by NMRTEC S.A.S for calculation of the dosy spectrum.

***In situ* reaction of the catalyst-capped macromolecular chain with benzophenone (run 1 given here as an example).** A standard polymerization of isoprene was conducted with $Nd(BH_4)_3(THF)_3$/BEM (Nd 17 µmol) as catalyst during 2 h at 50 °C in toluene (isoprene = 231 mg, 0.34 mL, 3.40 mmol; [isoprene]/[Nd] = 200). Without quenching the experiment, benzophenone (4 equiv *vs*. Nd) was added to the polymerization mixture and allowed to react at 50 °C for 12 h. The reaction was quenched with a few drops of acidified methanol. The polymer was recovered by precipitation in a large excess of methanol containing BHT as stabilizing agent, and dried under vacuum until constant weight (0.185 g, 80%, 96.9 % 1,4-*trans*-regular and 49 % end-functionalized).

***In situ* reaction with benzophenone with prior Coordinative Chain Transfer Polymerization (run 3 given here as an example).** A polymerization of isoprene was conducted under CCTP conditions, *ie* with $Nd(BH_4)_3(THF)_3$/BEM/$AlEt_3$ (Nd = Mg = 10 µmol, Al = 90 µmol) as catalyst at 50 °C in toluene (isoprene = 680 mg, 1 mL, 10 mmol; isoprene/Nd ratio = 1000). After a given time when the conversion is considered as complete, as seen by the green highly viscous medium (24 h for run 3), the reactor is transferred to the glovebox to add benzophenone (2 equiv per alkyl, 106 mg) to the mixture, which is allowed to stir for a given time (12 h) at a given temperature (50 °C). The polymer is recovered as detailed above (0.53 g, 78.3 %, 87.5 % 1,4-*trans*-regular and 81 % end-functionalized).

***In situ* reaction with benzophenone with prior Nd/Mg transfer of the macromolecular chain (run 5 given here as an example).** A standard polymerization of isoprene was conducted as described above for run 1. After a given time when the conversion is considered as complete (2 h), the reactor is transferred to the glovebox to add BEM in excess (10 fold equiv *vs*. Nd) to the reaction mixture. Then, the mixture is allowed to react at 50 °C under stirring for a given time (1 h). In the glove box, benzophenone (2 equiv per alkyl, 60 mg) is introduced into the reaction flask and the reaction is carried out under stirring for a given time at a given temperature (12 h, 50 °C). The polymer (76 %, polyisoprene 96.2 % 1,4-*trans*-regular and 89 % end-functionalized) is recovered as detailed above.

***In situ* reaction with benzophenone with prior Nd/Li transfer of the macromolecular chain (run 7 given as an example).** The same procedure as for run 5 is followed, but with *n*-BuLi in excess (20 fold equiv) instead of BEM as transfer reagent, affording 100 % polyisoprene 95.3 % 1,4-*trans*-regular and 92 % end-functionalized.

***In situ* reaction with benzaldehyde with prior Nd/Li transfer of the macromolecular chain (run 9 given as an example).** The same procedure as for run 5 is followed, but starting with 20.3 mg of $Nd(BH_4)_3(THF)_3$ (50 µmol) and with benzaldehyde instead of benzophenone as functionalization agent (20 equiv in THF). After 16 h at 50 °C and work-up, affording 680 mg (yield > 99%) of polyisoprene 98 % 1,4-*trans*-regular and 95 % end-functionalized.

***In situ* reaction with styrene oxide with prior Nd/Li transfer of the macromolecular chain (run 10 given as an example).** The same procedure as for run 5 is followed, but starting with 20.3 mg of $Nd(BH_4)_3(THF)_3$ (50 µmol) and with styrene oxide instead of benzophenone as functionalization agent (20 equiv in THF). After 16 h at 50 °C and work-up, affording 670 mg (yield > 98%) of polyisoprene 98 % 1,4-*trans*-regular and 96 % end-functionalized.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Additional figures

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S.G., O.H. and Y.C. experimental work and analyses, M.B. specific NMR experiments (DOSY), P.Z. and Y.C. supervision of experimental work and discussions, careful reading of the manuscript, M.V. writing of the manuscript, supervision of experimental work, complementary experiments and analyses, discussions.

Notes

The authors declare no competing financial interest.

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