

# Access to Highly Stereodefined 1,4-*cis*-Polydienes by a [Ni/Mg] Orthogonal Tandem Catalytic Polymerization

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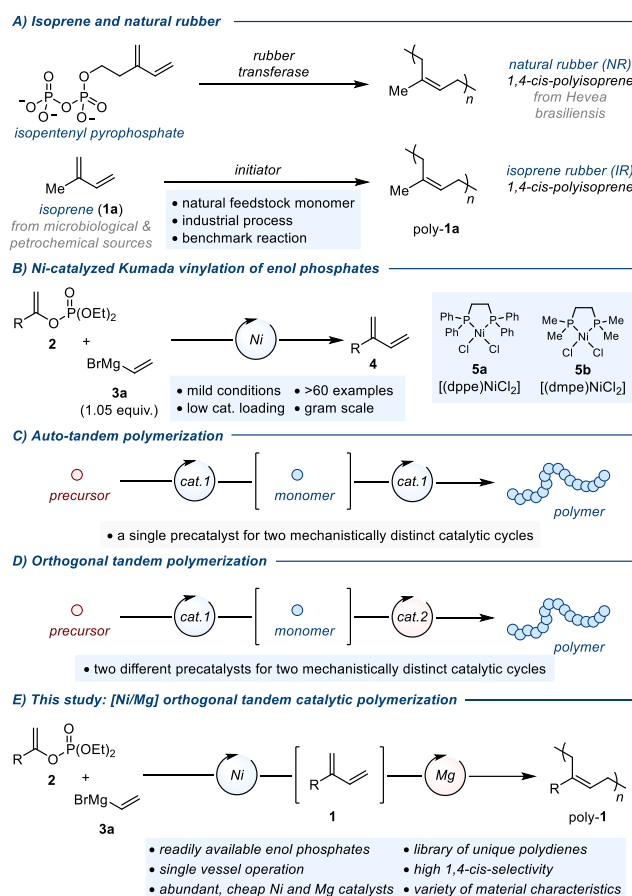
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**ABSTRACT:** A [Ni/Mg]-catalyzed orthogonal tandem polymerization has been developed starting from enol phosphates. Initial investigations conducted on branched 1,3-dienes as monomers enabled identification of a Mg-initiated polymerization process leading to 1,4-*cis*-polydienes. When aryl enol phosphates are used as monomers, the [Ni/Mg]-catalyzed tandem polymerization affords 1,4-*cis*-polydienes with selectivities up to 99%. Elastomeric or crystalline materials were obtained by simple structural modifications of the monomeric unit. This tandem approach appears as a straightforward and efficient way to enforce diversity and selectivity in diene polymerization while retaining a fair degree of control, just as observed for stepwise systems that are accessible through established time- and manpower-consuming synthetic procedures.

## ■ INTRODUCTION

Polydienes are commodity chemicals with countless industrial and medical applications.<sup>1</sup> More specifically, natural rubber (NR) is a high-molecular-weight valuable plant-derived poly(*cis*-1,4-isoprene) synthesized by a rubber *cis*-prenyltransferase complex (CPT).<sup>2</sup> Because extraction from natural sources cannot sustain the ever increasing global demand of NR, 1,4-*cis*-polyisoprene is produced industrially by polymerization of isoprene (IR). NR and IR have very similar properties.<sup>3</sup> Isoprene is also a naturally occurring compound, produced and emitted by a variety of animals and plants, but paradoxically it is not the monomer used by Nature for the production of NR. Over the past decades, chemical and engineering research on isoprene polymerization, both in academia and industry, has led to major advances in the fields of rubber technology and stereoselective polymerization. Nowadays, isoprene polymerization represents a benchmark reaction for every novel diene-polymerization initiator (Figure 1, A).<sup>4-7</sup> Aside from isoprene polymerization, and to a lesser extent myrcene polymerization, only scattered studies have focused on the homopolymerization of non-naturally occurring 2-substituted 1,3-dienes, a situation that can be ascribed to the limited synthetic availability of these building blocks until recently.<sup>8-10</sup> Consequently, the field clearly bears enormous potential because –aside from stereochemical considerations– subtle variations on the nature of the diene substituent are expected to strongly impact the macromolecular properties of the resulting polymer.

In 2018, one of our groups reported a Ni-catalyzed Kumada cross-coupling reaction between vinyl magnesium bromide and readily available vinyl phosphates.<sup>11</sup> Two distinct catalysts **5a** and **5b** with complementary reactivity profiles and wide functional group tolerance have been identified for the preparation of a broad diversity of 2-aryl and 2-alkyl 1,3-dienes (Figure 1, B). We subsequently



**Figure 1.** (A) Naturally occurring diene and polydiene. (B) Ni-catalyzed vinylation of enol phosphates. (C) Auto-tandem polymerization. (D) Orthogonal tandem polymerization. (E) [Ni/Mg] orthogonal tandem catalytic polymerization starting from enol phosphates.

initiated a program directed toward the use of 2-substituted dienes as a discovery platform for the devise of selective catalytic methods.<sup>12-13</sup> In this context, we initially set out to

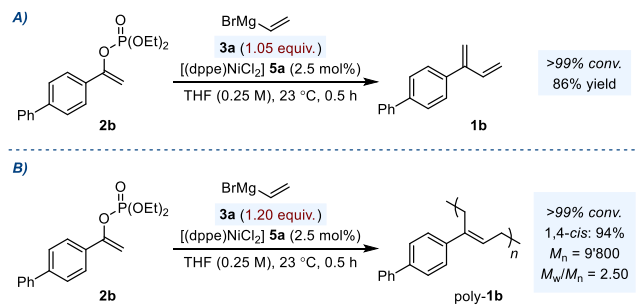
identify a Ni catalyst for the stereoselective polymerization of 2-substituted dienes with the primary idea of extending polydiene chemistry to the use of novel monomeric diene units. Our ultimate goal was to develop either (i) an auto-tandem catalytic polymerization process in which a single Ni precatalyst would perform two mechanistically distinct operations starting from simple enol phosphates (Figure 1, C), or (ii) an orthogonal tandem catalytic polymerization process (Figure 1, D). Realization of either strategy would undeniably lead to substantial time- and cost-savings, atom economy, waste reduction and decrease in energy consumption. While auto-tandem catalysis requires the identification of a ubiquity-gifted organometallic compound, orthogonal tandem catalysis necessitates two distinct highly reactive species to coexist in solution without any detrimental interactions.<sup>14,15</sup>

In this article, we disclose how pursuing our initial objective led to the serendipitous discovery of a one-pot [Ni/Mg] orthogonal tandem catalytic polymerization protocol (Figure 1, E). Starting from enol phosphates, the process combines a Ni-catalyzed Kumada cross-coupling, that produces 1,3-dienes in situ, with a Mg-initiated polymerization process that affords new 1,4-*cis* polydienes (up to 99%). In addition, the high functional diversity of the monomers obtained allows to easily tune the thermal properties of the corresponding materials, thus giving access to elastomeric polymers (classical for 1,4-*cis* polydienes) but also to crystalline polymers (generally observed for 1,4-*trans* polymers).

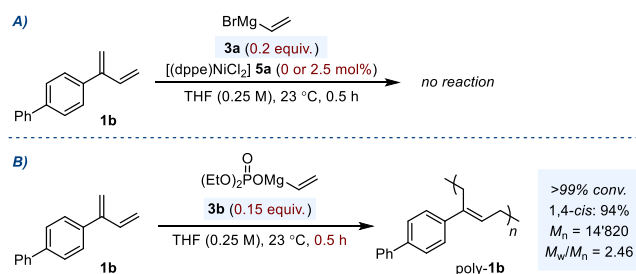
## RESULTS AND DISCUSSION

Our initial attempts were focused on the identification of late transition metal precatalysts for the polymerization of isolated 2-substituted 1,3-dienes using non-naturally occurring **1b** as model substrate. In the prototypical reaction conditions initially reported for the vinylation of enol phosphate **2b** using [(dppe)NiCl<sub>2</sub>] **5a** as precatalyst, a stoichiometric amount of vinyl magnesium bromide **3a** was used and **1b** was isolated in 86% yield (Figure 2, A).<sup>11</sup> We unintentionally found that when the reaction was conducted with a slight excess of **3a** (1.20 equiv.), with otherwise identical conditions, a polymeric material was formed quantitatively (Figure 2, B). The identity of the polymer (poly-**1b**) was established by <sup>1</sup>H and <sup>13</sup>C NMR analyses and revealed a predominant 1,4-*cis* microstructure (1,4-*cis* vs 1,2-microstructure = 93:7).<sup>8b-c, 10b</sup> To understand the origin of the polymerization process, a series of control experiments was conducted next (Figure 3). No reaction occurred when **1b** was subjected to catalysis using **5a** and a stoichiometry in vinyl magnesium bromide **3a** that corresponds to the excess in the reaction starting from enol phosphates **2b** (0.2 equiv.). Similarly, no polymer formation was observed in the absence of nickel precatalyst after 0.5 h (Figure 3, A).

We surmised that the magnesium phosphate salts generated during the Ni-catalyzed vinylation of **2b** may participate in the polymerization process (Figure 3, B). Our assumption was guided by the notion that Mg ions are directly involved in C–C bond forming events in isoprenyl diphosphate synthases (IDS), which produce long-chain Z-type isoprenoids, including natural rubber.<sup>16</sup> To test our



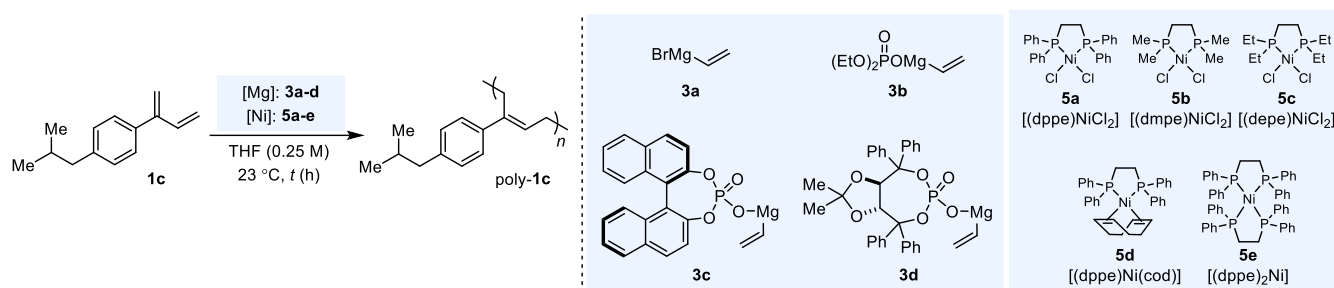
**Figure 2.** (A) Ni-catalyzed vinylation of enol phosphate **2b**. (B) Polymerization of **2b** into poly-**1b** under slightly modified reaction conditions.



**Figure 3.** Control experiments. (A) Attempted polymerization of **1b** using vinyl magnesium bromide **3a** as initiator. (B) Polymerization of **1b** using vinyl magnesium phosphate **3b**.

hypothesis, the independently synthesized vinyl magnesium phosphate **3b** was evaluated in the polymerization of **1b** (Figure 3, B). Pleasingly, within only 0.5 h, 1,4-*cis*-poly-**1b** was generated quantitatively with similar polymerization data than those of the previous experiment. We are not aware of prior examples of Mg-initiated polymerization of 1,3-dienes. Collectively, the results disclosed in Figures 2 and 3 point to an organomagnesium-initiated polymerization, a process that is usually achieved with BuLi or alkali-naphthalene for 2-aryl substituted 1,3-dienes.<sup>4, 8a-d</sup>

The identification of vinyl magnesium diethyl phosphate **3b** acting as initiator for the polymerization of diene **1b** prompted us to study this unusual process in more details. In order to perform a systematic analysis of the important reaction parameters on a more practical time scale, the less reactive diene **1c** was selected as test substrate (Table 1). In line with the result obtained with **1b**, when vinyl magnesium bromide **3a** was used as initiator in absence of a nickel precatalyst, no reaction occurred (Entry 1).<sup>17</sup> By contrast, similar reactivity and productivity were observed in the polymerization of **1b** using vinyl magnesium diethyl phosphate **3b** in combination with (dppe)-containing nickel precatalysts **5a**, **5d** and **5e** (Entries 2, 5–6). In all cases, poly-1,4-*cis*-**1c** was obtained with a relatively narrow range of  $M_n$  (20'600–23'960 g·mol<sup>-1</sup>) and dispersities (1.71–1.76). While the use of **5b** led to a reduced  $M_n$ , no polymerization was observed with **5c** (Entries 3–4). The impact of the nature of the phosphine ligand in complexes **5a–e** on the overall outcome of the process suggests a possible –yet unidentified– interplay between Mg and Ni. Based on the assumption that two equivalents of **3b** are necessary to activate the Ni(II) complex **5a** by a double transmetalation/reductive elimination sequence, for these

**Table 1. Diene polymerization optimization**

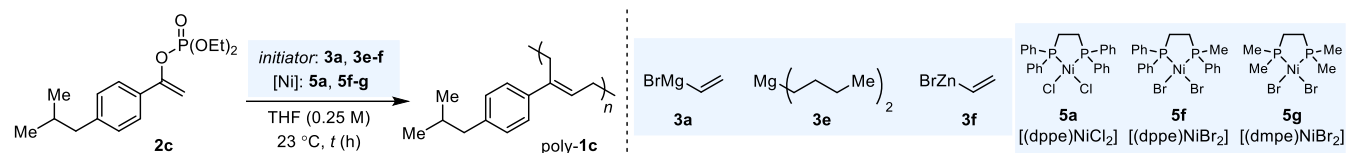
Entry	[Ni]	[Mg]	[Mg]/[ <b>1c</b> ]	[Mg]/[Ni]	<i>t</i> (h)	Conv. (%) <sup>a</sup>	<i>M<sub>n</sub></i> (g.mol <sup>-1</sup> ) <sup>b</sup>	<i>Đ</i> <sup>b</sup>	1,4- <i>cis</i> (%) <sup>c</sup>
1	-	<b>3a</b>	1/6.7	1/0	24	<1	-	-	-
2	<b>5a</b>	<b>3b</b>	1/5	8/1	2.0	75	20'600	1.76	93
3	<b>5b</b>	<b>3b</b>	1/5	8/1	5.0	88	13'000	1.71	93
4	<b>5c</b>	<b>3b</b>	1/5	8/1	16.0	<1	-	-	-
5	<b>5d</b>	<b>3b</b>	1/6.7	6/1	5.5	67	22'220	1.76	93
6	<b>5e</b>	<b>3b</b>	1/6.7	6/1	4.5	82	23'350	1.76	93
7	<b>5a</b>	<b>3b</b>	1/13.3	3/1	5.5	85	32'800	1.91	93
8	<b>5a</b>	<b>3b</b>	1/40	1/1	16.0	<1	-	-	-
9	<b>5e</b>	<b>3b</b>	1/40	1/1	21.0	93	38'200	2.25	93
10	-	<b>3b</b>	1/6.7	1/0	5.5	85	23'600	1.82	93
11 <sup>d</sup>	-	<b>3b</b>	1/6.7	1/0	3.75	78	22'300	1.75	86
12	-	<b>3b</b>	1/40	1/0	5.5	93	41'400	2.0	93
13	-	<b>3c</b>	1/6.7	1/0	5.5	61	5'100	2.43	94
14	-	<b>3d</b>	1/6.7	1/0	5.5	82	26'000	1.85	93

Reaction performed on a 0.15 mmol scale at 23 °C. <sup>a</sup> Conversion determined by <sup>1</sup>H NMR spectroscopy. <sup>b</sup> *M<sub>n</sub>* and *Đ* of polymer determined on crude polymers by SEC-RI in THF at 35 °C using polystyrene standards. <sup>c</sup> Polymer microstructure determined by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. <sup>d</sup> [**1c**] = 1.0 M.

experiments the [Mg]/[Ni] ratio was gradually adjusted taking into account the oxidation state of the nickel complex (Entries 7–8). Quite notably, in the absence of a nickel source, a reactivity similar to that achieved with the *dppe*-based nickel complexes was observed. A higher monomer concentration led to an increased efficiency, albeit at the expense of 1,4-*cis* control (Entries 10–11). When a higher ratio of magnesium to monomer was used ([Mg]/[**1c**] = 1/40), the number average molecular weight of the polymer increased up to 41 400 g.mol<sup>-1</sup> (Entry 12). A retrospective comparison between Entry 8, 9 and 12 suggests that when an equimolar amount of the Ni(II) precatalyst and Mg precursor is employed, the double transmetalation step of the activation process may occur more readily and consume all potential initiating vinyl-containing Mg species. In line with this hypothesis, polymerization also occurred with alternative vinyl magnesium phosphates **3c–3d** (Entries 13–14).

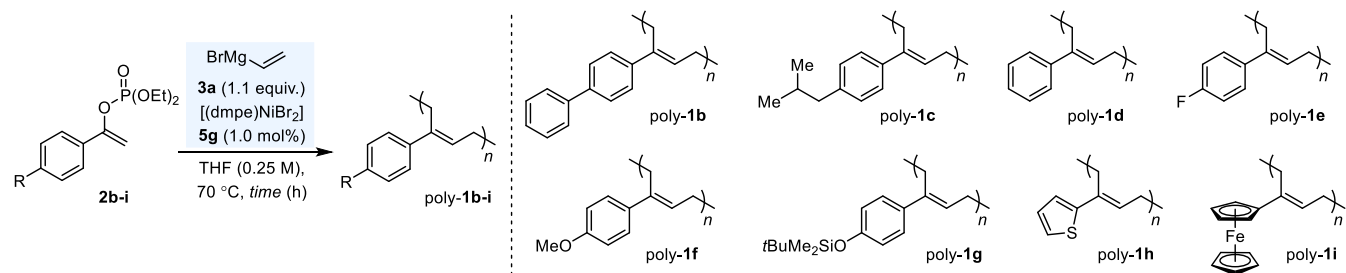
We next investigated the *orthogonal tandem* catalytic transformation of enol phosphate **2c** into poly-**1c**. The results are summarized in Table 2. To evaluate the feasibility of the overall process, we conducted preliminary experiments with nickel precatalyst **5a** in the presence of **3a** as initiator. This complex proved to be an active initiator for the polymerization of in situ generated diene **1b** to obtain poly-**1b** with high level of 1,4-*cis* selectivity (93%; Entry 1). Of note, a similar reactivity was achieved for a

*sequential* reaction where 0.15 equivalents of *n*Bu<sub>2</sub>Mg **3e** were added after the vinylation step with vinyl magnesium bromide (1.05 equiv.; Entry 2).<sup>19</sup> However, no polymerization occurred with vinyl zinc bromide **3f**, even with prolonged reaction times. Instead, diene **1c** was generated quantitatively in 0.5 h (Entry 3). The catalytic system was further optimized by fine-tuning different parameters. Two tandem reactions using **3a** as initiator afforded high conversions and fairly narrow dispersities from a monomer prepared with **5f** and **5g** (Entries 4–5). Higher masses were obtained by increasing the [Mg]/[Ni] ratio (Entry 6). When the polymerization temperature was increased to 50 °C, we observed enhanced activity and regioselectivity using either the **5f/3a** system or the **5g/3a** combination (Entries 7–8). A 1,4-*cis* polymer with 99% selectivity was obtained with the latter when the reaction was conducted at 70 °C (Entry 9). Finally, reaction monitoring at 50 °C (Entry 8) revealed a typical chain-growth behavior with a linear increase of *M<sub>n</sub>* over time ( $\rho = 64.7$ ,  $R^2 = 0.99$ ), and negligible variation of dispersity (see Supporting Information, Figure S3). MALDI-TOF mass spectrometry analyses of polymer samples obtained from the tandem catalytic system (Table 2, Entry 1) consistently showed a peak distribution corresponding to polymer chains terminated by a vinyl moiety, thus confirming its role as an initiating group (See Supporting Information for details).

**Table 2. Tandem vinylation/diene polymerization**

Entry	[Ni]	Initiator	[Initiator]/[ <b>2c</b> ] <sup>a</sup>	[Initiator]/[Ni]	$t$ (h)	Conv. (%) <sup>b</sup>	$M_n$ (g.mol <sup>-1</sup> ) <sup>c</sup>	$\bar{D}$ <sup>c</sup>	1,4- <i>cis</i> (%) <sup>d</sup>
1	<b>5a</b>	<b>3a</b>	1/6.7	6/1	6	53	5'700	1.73	93
2 <sup>f</sup>	<b>5a</b>	<b>3e</b>	1/6.7	6/1	14	77	7'900	1.68	93
3	<b>5a</b>	<b>3f</b>	1/6.7	6/1	48	<1	-	-	-
4	<b>5f</b>	<b>3a</b>	1/6.7	6/1	6	87	6'000	1.75	93
5	<b>5g</b>	<b>3a</b>	1/6.7	6/1	6	94	4'300	1.65	93
6	<b>5g</b>	<b>3a</b>	1/5.3	38/1	16	97	10'300	1.65	93
7 <sup>g</sup>	<b>5f</b>	<b>3a</b>	1/6.7	6/1	6	>99	3'400	1.38	97
8 <sup>g</sup>	<b>5g</b>	<b>3a</b>	1/12.5	8/1	4	66	4'800	1.54	97
9 <sup>h</sup>	<b>5g</b>	<b>3a</b>	1/12.5	8/1	4	67	3'700	1.53	99

Reactions performed on a 0.15 mmol scale. <sup>a</sup> Ratio related to the polymerization step after the Ni-catalyzed vinylation in the tandem process by assuming complete conversion of **2c** into **1c**. Initial ratio: [initiator]/[**2c**] = 1.05/1; [initiator]/[Ni] = 48/1. <sup>b</sup> Conversion determined by <sup>1</sup>H NMR spectroscopy. <sup>c</sup>  $M_n$  and  $\bar{D}$  of polymer determined by SEC-RI on crude polymers in THF at 35 °C using polystyrene standards. <sup>d</sup> Polymer microstructure determined by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy. <sup>f</sup> Reaction conducted as a one-pot sequence: **3a** used to generate diene **1c** in situ and **3e** added after the vinylation step ([**3a**]/[Ni] = 48/1; [**3a**]/[**2c**] = 1.05/1; 0.5 h, then [**3e**]/[Ni] = 6/1; [**3e**]/[**2c**] = 1/6.7). <sup>g</sup> Reaction performed at 50 °C. <sup>h</sup> Reaction performed at 70 °C.

**Table 3. Tandem polymerization of various enol phosphates**

Entry	Polymer	$t$ (h)	Conv. (%) <sup>a</sup>	$M_n$ (g.mol <sup>-1</sup> ) <sup>b</sup>	$\bar{D}$ <sup>b</sup>	1,4- <i>cis</i> (%) <sup>c</sup>	$T_g$ (°C) <sup>d</sup>	$T_m$ (°C) <sup>d</sup>
1 <sup>e</sup>	poly- <b>1b</b>	1	95 (60)	6'800	2.27	96	79	216
2 <sup>e</sup>	poly- <b>1c</b>	24	95 (70)	14'500	1.94	93	18	-
3	poly- <b>1d</b>	1	90 (57)	2'700	1.84	98	29	-
4	poly- <b>1e</b>	4	90 (70)	5'200	1.84	>99	32	-
5 <sup>e</sup>	poly- <b>1f</b>	1	99	2'100	1.66	94	31	-
6	poly- <b>1g</b>	7	56 (51)	4'400	1.31	97	37	-
7	poly- <b>1h</b>	1	95 (75)	1'900	3.41	92	<i>nd</i> <sup>f</sup>	-
8	poly- <b>1i</b>	4	94 (56)	1'100	1.37	79	64	-

Reactions performed on a 0.3-0.6 mmol scale. <sup>a</sup> Conversion into **poly-1** determined by <sup>1</sup>H NMR spectroscopy. The remainder consists of unreacted diene exclusively. In parenthesis, isolated yield of pure material after precipitation in MeOH. <sup>b</sup>  $M_n$  and  $\bar{D}$  of purified polymer determined by SEC-RI in THF at 35 °C using polystyrene standards. <sup>c</sup> Polymer microstructure determined by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy on purified polymers. <sup>d</sup>  $T_g$  and  $T_m$  of purified polymer determined by DSC on second heating cycle (10 °C/min, N<sub>2</sub> flow). <sup>e</sup> [(dppe)NiCl<sub>2</sub>] **5a** (2.5 mol%), vinyl magnesium bromide **3a** (1.2 equiv.), 23 °C. <sup>f</sup> Not determined.

The optimized conditions for the tandem [Mg]/[Ni] process were applied to a small set of enol phosphates for the preparation of the corresponding polymers (Table 3). These new materials were characterized by differential scanning calorimetry (DSC) and thermogravimetric

analysis (TGA) (Table 3 & SI). The broad range of glass transition temperatures ( $T_g$ ) recorded confirms the wide variety of characteristics that can be obtained by our synthetic method. Indeed, glass transition temperatures varied from 18 to 79 °C by simple permutation of the

functional group in *para* position of the aryl ring (Entries 1–6). Quite notably, when a *para*-phenyl substituent was introduced as in **2b**, the corresponding polymer poly-**1b** was obtained as a crystalline material which displayed a melting temperature of 216 °C (Entry 1). This substitution pattern clearly influences the polymer degradation temperature since poly-**1b** showed only a marginal 5% weight loss at 296 °C. This unusual stability provides a better processability to the final material because the operational window between the melting temperature and the degradation temperature is significantly expanded. Functional groups such as fluorine, ethers and thiophene were well tolerated under the tandem reaction conditions (Entries 4–7), giving access to functionalized polymers with good to excellent 1,4-*cis* stereoselectivity.<sup>10</sup> Finally, a ferrocenyl-containing polydiene (poly-**1i**, Entry 8) was readily prepared in two steps from commercially available acetyl ferrocene, thus highlighting the extent of molecular diversity accessible with the present approach.<sup>20,21</sup>

## CONCLUSION

In summary, in this contribution we disclosed the serendipitous discovery of a one-pot [Ni/Mg] orthogonal tandem catalytic polymerization protocol starting from readily available enol phosphates. Initial investigations have been conducted on branched dienes as monomeric units and served to identify an unorthodox Mg-initiated polymerization process leading to 1,4-*cis*-polydienes with a relatively narrow range of  $M_n$  (20'600–23'960 g.mol<sup>-1</sup>) and dispersities (1.71–1.76). Even though polymerization occurred with the sole use of vinyl magnesium phosphate derivatives, systematic variations of the Mg initiator and of the structure of the nickel catalyst point to an interplay between both components.<sup>22</sup> The exact nature of this interaction remains unclear at this stage. The one-pot [Ni/Mg] orthogonal tandem catalytic polymerization protocol starting from aryl enol phosphates was developed next. The system combines a [(P,P)Ni(II)] complex with a Mg initiator and produces 1,4-*cis*-polydienes with selectivities up to 99% when the reaction is conducted at 70 °C. The availability and modularity of the enol phosphate monomers permitted adjusting the thermal properties of the corresponding polymers, ranging from elastomeric to crystalline materials. While the former are expected for 1,4-*cis* polydienes, the latter are usually observed for 1,4-*trans* polymers. Current efforts in our laboratories are directed toward understanding the origin of the interaction between the Mg initiator and the Ni precatalyst as well as expanding the scope of applications of this tandem protocol.

## ASSOCIATED CONTENT

**Supporting Information.** Experimental procedures, characterization of all new compounds, spectroscopic, spectrometric and SEC, DSC and TGA analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENT

We thank the University of Geneva, the Swiss National Science Foundation (project 200021\_159199), Chimie ParisTech and the Institut Universitaire de France for financial support. We would like to thank Dr. N. Soliman (PSL University) for GPC analyses and Dr. C. Robert (PSL University) for MALDI-TOF analyses. We thank Dr. G. Tran (University of Geneva) for conducting preliminary experiments and for fruitful scientific discussions.

## REFERENCES

- (1) *Rubber Technologist's Handbook*. Eds. De, S. K.; White, J. R. Rapra Technology Limited: Shawbury, UK, **2001**.
- (2) Mann, C. C. Addicted to Rubber. *Science* **2009**, *325*, 564.
- (3) (a) Greve, H. H. Rubber, 2. Natural. Ullmann's Encyclopedia of Industrial Chemistry; Wiley-VCH: Weinheim, 2000. (b) Threadingham, D.; Obrecht, W.; Wieder, W.; Wachholz, G.; Engehausen, R. Rubber, 3. Synthetic Rubbers, Introduction and Overview. In Ullmann's Encyclopedia of Industrial Chemistry; WileyVCH Verlag GmbH & Co. KGaA: Weinheim, 2000.
- (4) For anionic polymerization of isoprene, see: Hirao, A.; Takenaka, K. Nonpolar Monomers: Styrene and 1,3-Butadiene Derivatives. In Anionic Polymerization. Principles, Practice, Strength, Consequences and Applications. Hadjichristidis, N.; Hirao, A. Eds, Springer 2015. p. 61-126.
- (5) For cationic polymerization of isoprene, see: Ouardad, S.; Bakleh, M.-E.; Kostjuk, S. V.; Ganachaud, F.; Puskas, J. E.; Deffieux, A.; Peruch, F. Bio-Inspired Cationic Polymerization of Isoprene and Analogues: State-of-the-Art. *Polym. Int.* **2012**, *61*, 149.
- (6) For coordination-insertion polymerization of dienes, see: (a) Osakada, K.; Takeuchi, D. Coordination Polymerization of Dienes, Allenes, and Methylene-cycloalkanes. *Adv. Polym. Sci.* **2004**, *171*, 137. (b) Friebe, L.; Nuyken, O.; Obrecht, W. Neodymium-Based Ziegler/ Natta Catalysts and their Application in Diene Polymerization. *Adv. Polym. Sci.* **2006**, *204*, 1. (c) Ricci, G.; Sommazzi, A.; Masi, F.; Ricci, M.; Boglia, A.; Leone, G. Well-Defined Transition Metal Complexes with Phosphorus and Nitrogen Ligands for 1,3-Dienes Polymerization. *Coord. Chem. Rev.* **2010**, *254*, 661. (d) Nishiura, M.; Hou, Z. Novel Polymerization Catalysts and Hydride Clusters from Rare-Earth Metal Dialkyls. *Nat. Chem.* **2010**, *2*, 257. (e) Huang, J. M.; Liu, Z. H.; Cui, D. M.; Liu, X. L. Precisely Controlled Polymerization of Styrene and Conjugated Dienes by Group 3 Single-Site Catalysts. *ChemCatChem* **2018**, *10*, 42. (f) Zhao, J.; Chen, H.; Li, W.; Jia, X.; Zhang, X.; Gong, D. Polymerization of Isoprene Promoted by Aminophosphine(ory)-Fused Bipyridine Cobalt Complexes: Precise Control of Molecular Weight and *cis*-1,4-*alt*-3,4 Sequence. *Inorg. Chem.* **2018**, *57*, 4088.
- (7) For radical polymerization of isoprene, see: Moad, G.; Solomon, D. H. *The Chemistry of Radical Polymerization*; Elsevier: Amsterdam, 2005. p. 182-184.
- (8) For anionic polymerization of unnatural 2-substituted dienes, see: (a) Stille, J. K.; Vessel, E. D. Polymerization of Phenyl-Substituted Butadienes by Metal Alkyl Catalysts. *J. Polym. Sci.* **1961**, *49*, 419. (b) Ambrose, R. J.; Hergenrother, W. L. Structure of Anionic Poly(2-phenylbutadiene). *Macromolecules* **1972**, *5*, 275. (c) Suzuki, T.; Tsuji, Y.; Takegami, Y.; Harwood, H. J. Microstructure of Poly(2-Phenylbutadiene) Prepared by Anionic Initiators. *Macromolecules* **1979**, *12*, 234. (d) Takenaka, K.; Hirao, A.; Hattori, T.; Nakahama, S. Polymerization of Monomers Containing Functional Silyl Groups. 4. Anionic Polymerization of 2-(Trimethoxysilyl)-1,3-Butadiene. *Macromolecules* **1987**, *20*, 2034. For cationic polymerization, see: (e) Hasegawa, K.; Asami, R.; Higashimura, T. Cationic Polymerization of Alkyl-1,3-butadienes. *Macromolecules* **1977**, *10*, 592. For coordination-insertion polymerization, see: (f) Pragliola,

- S.; Cipriano, M.; Boccia, A. C.; Longo, P. Polymerization of Phenyl-1, 3-Butadienes in the Presence of Ziegler-Natta Catalysts. *Macromol. Rapid Commun.* **2002**, *23*, 356. (g) Long, S.; Lin, F.; Yao, C.; Cui, D. Highly cis-1,4 Selective Living Polymerization of Unmasked Polar 2-(2-Methylidenebut-3-enyl)Furan and Diels-Alder Addition. *Macromol. Rapid Commun.* **2017**, *38*, 1700227. For radical polymerization, see: (h) Takenaka, K.; Hanada, K.; Shiomi, T. Polymerization of 1,3-Dienes with Functional Groups. 1. Free-Radical Polymerization of 2-Triethoxymethyl-1,3-butadiene. *Macromolecules* **1999**, *32*, 3875. (i) Jing, Y.; Sheares, V. V. Polar, Functionalized Diene-based Materials. 1. Bulk, Dolution, and Emulsion Free Radical Polymerization of 2-Cyanomethyl-1, 3-utadiene. *Macromolecules* **2000**, *33*, 6255. (j) Sheares, V. V.; Wu, L. F.; Li, Y. X.; Emmick, T. K. Polar, Functionalized Diene-based Material. III. Free-Radical Polymerization of 2-[(N,N-Dialkylamino)methyl]-1,3-butadienes. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4070. (k) Kobayashi, S.; Kataoka, H.; Ishizone, T. Synthesis of Well-Defined Poly(ethylene-alt-1-vinyladamantane) via Living Anionic Polymerization of 2-(1-Adamantyl)-1,3-butadiene, Followed by Hydrogenation. *Macromolecules* **2009**, *42*, 5017.
- (9) (a) Qi, Y.; Liu, Z.; Liu, S.; Cui, L.; Dai, Q.; He, J.; Dong, W.; Bai, C. Synthesis of 1, 3-Butadiene and its 2-Substituted Monomers for Synthetic Rubbers. *Catalysts* **2019**, *9*, 97. (b) Ricci, G.; Pampaloni, G.; Somazzi, A.; Masi, F. Dienes Polymerization: Where We Are and What Lies Ahead. *Macromolecules* **2021**, *54*, 5879.
- (10) For copolymerization of butadiene and isoprene with functionalized dienes, see: (a) Leicht, H.; Göttker-Schnetmann, I.; Mecking, S. Stereoselective Copolymerization of Butadiene and Functionalized 1,3-Dienes. *ACS Macro Lett.* **2016**, *5*, 777. (b) Yao, C.; Liu, N.; Long, S.; Wu, C.; Cui, D. Highly cis-1,4-selective Coordination Polymerization of Polar 2-(4-methoxyphenyl)-1,3-butadiene and Copolymerization with Isoprene Using a  $\beta$ -Diketiminato Yttrium Bis(alkyl) Complex. *Polym. Chem.* **2016**, *7*, 1264. (c) Leicht, H.; Göttker-Schnetmann, I.; Mecking, S. Synergetic Effect of Monomer Functional Group Coordination in Catalytic Insertion Polymerization. *J. Am. Chem. Soc.* **2017**, *139*, 6823. (d) Tang, M.; Zhang, R.; Li, S.; Zeng, J.; Luo, M.; Xu, Y. X.; Huang, G. Towards a Supertough Thermoplastic Polyisoprene Elastomer Based on a Biomimic Strategy. *Angew. Chem., Int. Ed.* **2018**, *57*, 15836. (e) Cai, L.; Long, S.; Wu, C.; Li, S.; Yao, C.; Hua, X.; Na, H. Liu, D.; Tang, T.; Cui, D. Highly Selective cis-1, 4 Copolymerization of Dienes with Polar 2-(3-methylidenebut-4-en-1-yl) Pyridine: an Approach for Recyclable Elastomers. *Polym. Chem.* **2020**, *11*, 1646.
- (11) Fiorito, D.; Folliet, S.; Liu, Y.; Mazet, C. A General Nickel-Catalyzed Kumada Vinylation for the Preparation of 2-Substituted 1, 3-Dienes. *ACS Catal.* **2018**, *8*, 1392.
- (12) For relevant reviews, see: (a) Herrmann, N.; Vogelsang, D.; Behr, A.; Seidensticker, T. Homogeneously Catalyzed 1,3-Diene Functionalization—A Success Story from Laboratory to Miniplant Scale. *ChemCatChem* **2018**, *10*, 5342. (b) Xiong, Y.; Sun, Y.; Zhang, G. Recent Advances on Catalytic Asymmetric Difunctionalization of 1,3-Dienes. *Tetrahedron Lett.* **2018**, *59*, 347. (c) Adamson, N. J.; Malcolmson, S. J. Catalytic Enantio- and Regioselective Addition of Nucleophiles in the Intermolecular Hydrofunctionalization of 1,3-Dienes. *ACS Catal.* **2020**, *10*, 1060. (d) Perry, G. J. P.; Jia, T.; Procter, D. J. Copper-Catalyzed Functionalization of 1,3-Dienes: Hydrofunctionalization, Borofunctionalization, and Difunctionalization. *ACS Catal.* **2020**, *10*, 1485.
- (13) (a) Liu, Y.; Fiorito, D.; Mazet, C. Copper-Catalyzed Enantioselective 1,2-Borylation of 1,3-Dienes. *Chem. Sci.* **2018**, *9*, 5284. (b) Fiorito, D.; Mazet, C. Ir-Catalyzed Selective Hydroboration of 2-Substituted 1,3-Dienes: A General Method to Access Homoallylic Boronates. *ACS Catal.* **2018**, *8*, 9382. (c) Tran, G.; Shao, W.; Mazet, C. Ni-Catalyzed Enantioselective Intermolecular Hydroamination of Branched 1,3-Dienes Using Primary Aliphatic Amines. *J. Am. Chem. Soc.* **2019**, *141*, 14814. (d) Tran, G.; Mazet, C. Ni-Catalyzed Regioselective Hydroalkoxylation of Branched 1,3-Dienes. *Org. Lett.* **2019**, *21*, 9124. (e) Garbo, M.; Besnard, C.; Guénee, L.; Mazet, C. Access to Optically Active 7-Membered Rings by a 2-Step Synthetic Sequence: Cu-Catalyzed Stereoselective Cyclopropanation of Branched 1,3-Dienes/Rh-Catalyzed Stereoconvergent [5 + 2] Cycloaddition. *ACS Catal.* **2020**, *10*, 9604. (f) Shao, W.; Besnard, C.; Guénee, L.; Mazet, C. Ni-Catalyzed Regiodivergent and Stereoselective Hydroalkylation of Acyclic Branched Dienes with Unstabilized C(sp<sup>3</sup>) Nucleophiles. *J. Am. Chem. Soc.* **2020**, *142*, 16486.
- (14) (a) Fogg, D. E.; Dos Santos, E. N. Tandem Catalysis: a Taxonomy and Illustrative Review. *Coord. Chem. Rev.* **2004**, *248*, 2365. (b) Robert, C.; Thomas, C. M. Tandem Catalysis: a New Approach to Polymers. *Chem. Soc. Rev.* **2013**, *42*, 9392. (c) Lohr, T. L.; Marks, T. J. Orthogonal Tandem Catalysis. *Nat. Chem.* **2015**, *7*, 477. (d) Peterson, G. I.; Choi, T.-L. Cascade Polymerizations: Recent Developments in the Formation of Polymer Repeat Units by Cascade Reactions. *Chem. Sci.* **2020**, *11*, 4843. (e) Fiorito, D.; Scaringi, S.; Mazet, C. Transition Metal-Catalyzed Alkene Isomerization as an Enabling Technology in Tandem, Sequential and Domino Processes. *Chem. Soc. Rev.* **2021**, *50*, 1391.
- (15) For selected examples of tandem catalysis in polymerization, see: (a) Crivello, J. V.; Rajaraman, S. K. Tandem Transition Metal Catalyzed Isomerization and Cationic Polymerization. *Macromol. Symp.* **1998**, *132*, 37. (b) Duxbury, C. J.; Wang, W.; de Geus M.; Heise, A.; Howdle, S. M. Can Block Copolymers Be Synthesized by a Single-Step Chemoenzymatic Route in Supercritical Carbon Dioxide? *J. Am. Chem. Soc.* **2005**, *127*, 2384. (c) van As, B. A. C.; van Buijtenen, J.; Heise, A.; Broxterman, Q. B.; Verzijl, G. K. M.; Palmans, A. R. A.; Meijer, E. W. Chiral Oligomers by Iterative Tandem Catalysis. *J. Am. Chem. Soc.* **2005**, *127*, 9964. (d) Camm, K. D.; Martinez Castro, N.; Liu, Y.; Czechura, P.; Snelgrove, J. L.; Fogg, D. E. Tandem ROMP-Hydrogenation with a Third-Generation Grubbs Catalyst. *J. Am. Chem. Soc.* **2007**, *129*, 4168. (e) Geng, J.; Lindqvist, J.; Mantovani, G.; Haddleton, D. M. Simultaneous Copper(I)-Catalyzed Azide-Alkyne Cycloaddition (CuAAC) and Living Radical Polymerization. *Angew. Chem., Int. Ed.* **2008**, *47*, 4180. (f) Dunn, E. W.; Coates, G. W. Carbonylative Polymerization of Propylene Oxide: A Multicatalytic Approach to the Synthesis of Poly(3-Hydroxybutyrate). *J. Am. Chem. Soc.* **2010**, *132*, 11412. (g) Robert, C.; de Montigny, F.; Thomas, C. M. Tandem Synthesis of Alternating Polyesters from Renewable Resources. *Nat. Commun.* **2011**, *2*, 586. (h) Park, H.; Choi, T.-L. Fast Tandem Ring-Opening/Ring-Closing Metathesis Polymerization from a Monomer Containing Cyclohexene and Terminal Alkyne. *J. Am. Chem. Soc.* **2012**, *134*, 7270. (i) Wu, G.-P.; Darensbourg, D. J.; Lu, X.-B. Tandem Metal-Coordination Copolymerization and Organocatalytic Ring-Opening Polymerization via Water to Synthesize Diblock Copolymers of Styrene Oxide/CO<sub>2</sub> and Lactide. *J. Am. Chem. Soc.* **2012**, *134*, 17739. (j) Raman, S. K.; Brule, E.; Tschan, M. J.-L.; Thomas, C. M. Tandem Catalysis: a New Approach to Polypeptides and Cyclic Carbonates. *Chem. Commun.* **2014**, *50*, 13773. (k) Nagarkar, A.; Yasir, M.; Crochet, A.; Fromm, K. M.; Kilbinger, A. F. M. Tandem Ring-Opening Ring Closing Metathesis for Functional Metathesis Catalysts. *Angew. Chem., Int. Ed.* **2016**, *55*, 12343. (l) Lee, H.-K.; Lee, J.; Kockelmann, J.; Herrmann, T.; Sarif, M.; Choi, T.-L. Superior Cascade Ring-Opening/Ring-Closing Metathesis Polymerization and Multiple Olefin Metathesis Polymerization: Enhancing the Driving Force for Successful Polymerization of Challenging Monomers. *J. Am. Chem. Soc.* **2018**, *140*, 10536. (m) Yasir, M.; Kilbinger, A. F. M. Cascade Ring-Opening/Ring-Closing Metathesis Polymerization of a Monomer Containing a Norbornene and a Cyclohexene Ring. *ACS Macro Lett.* **2021**, *10*, 210. (n) Fouilloux, H.; Qiang, W.; Robert, C.; Placet, V.; Thomas, C. M. Multicatalytic Transformation of (Meth)acrylic Acids: a One-Pot Approach to Biobased Poly(meth)acrylates. *Angew. Chem. Int. Ed.* **2021**, 10.1002/anie.202106640.
- (16) Chen, C.-C.; Zhang, L.; Yu, X.; Ma, L. Ko, T.-P.; Guo, R.-T. Versatile Cis-Isoprenyl Diphosphate Synthase Superfamily Members in Catalyzing Carbon-Carbon Bond Formation. *ACS Catal.* **2020**, *10*, 4717.

(17) Several organomagnesium and organoaluminum reagents were found to be inactive in the polymerization of diene **1c**. See Supporting Information for details (Figure S1).

(18) Diethyl enol phosphate **2c** was exclusively competent in the tandem polymerization described here. Other electrophiles, such as the corresponding diphenyl enol phosphate and vinyl bromide, led to the formation of diene **1c** via Kumada cross-coupling, with no traces of polymerization. See Supporting Information for details (Figure S2).

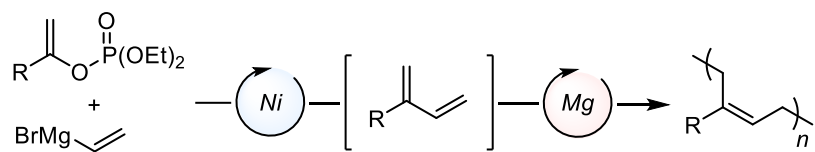
(19) Sequential addition of other organomagnesium reagents led to polymer formation, while no polymerization was observed for the sequential addition of alkyllithium and alkylaluminum reagents. See Supporting Information for details (Table S1).

(20) Pietschnig, R. Polymers with Pendant Ferrocenes. *Chem. Soc. Rev.* **2016**, *45*, 5216.

(21) (a) Lewis, D. H.; Kneisel, R. C.; Ponder, B. W. Free-Radical Polymerization of 1-Ferrocenyl-1,3-Butadiene and 1-Phenyl-1,3-Butadiene. Reactivity Ratios and Q and e Values. *Macromolecules* **1973**, *6*, 660. (b) Huskins, C. W.; Van Landuyt, D. C. Propellant

Compositions with Ferrocene Homo-Polymer. US Patent Office 3,843,426, **1974**.

(22) Although drawing definitive mechanistic conclusions is premature at this stage of our investigations, a plausible explanation to explain the origin of this orthogonal tandem polymerization process may lie in the ability of the nickel complexes to act as a reservoir of polymer chains that can be transmetallated to magnesium, which itself acts as active initiator. This exchange process may also explain the lower Mn obtained in the tandem process compared to direct diene polymerization. See: Valente, A.; Mortreux, A.; Visseaux, M.; Zinck, P. Coordinative chain transfer polymerization. *Chem. Rev.* **2013**, *113*, 3836.



- readily available enol phosphates
  - single vessel operation
  - abundant, cheap Ni and Mg catalysts
  - library of unique polydienes
  - high 1,4-cis-selectivity
  - variety of material characteristics
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