Polymerization

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Stereo- and Temporally Controlled Coordination Polymerization Triggered by Alternating Addition of a Lewis Acid and Base

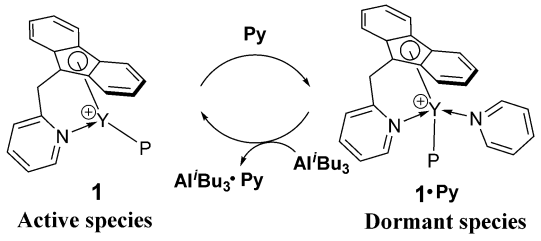
Bo Liu, Dongmei Cui, and Tao Tang*

Abstract: *Significant progress has been made with regard to temporally controlled radical and ring-opening polymerizations, for example, by means of chemical reagents, light, and voltage, whereas quantitative switch coordination polymerization is still challenging. Herein, we report the temporally and stereocontrolled 3,4-polymerization of isoprene through allosterically regulating the active metal center by alternating addition of Lewis basic pyridine to "poison" the Lewis acidic active metal species through acid–base interactions and Lewis acidic Al^iBu_3 to release the original active species through pyridine abstraction. This process is quick, quantitative, and can be repeated multiple times while maintaining high 3,4-selectivity. Moreover, this strategy is also effective for the switch copolymerization of isoprene and styrene with dual 3,4- and syndiotactic selectivity. Tuning the switch cycles and intervals enables the isolation of various copolymers with different distributions of 3,4-polyisoprene and syndiotactic polystyrene sequences.*

Inspired by syntheses of biomacromolecules with flawless primary microstructures in natural systems, repeatedly stopping and restarting polymerization by means of external stimuli ("temporally and spatially controlled polymerization") has been considered as an attractive method of regulating monomer sequences to enhance the physicochemical properties and functionalities of synthetic polymers.[1] Significant progress has been achieved for temporally controlled polymerization, for example, by ring opening polymerization (ROP) of lactides and cyclic esters,[2] atom transfer radical polymerization (ATRP) of acrylates,[3] and reversible addition fragmentation chain transfer (RAFT) polymerization of acrylates, styrene, and other polar vinyl monomers.[4] These processes are controlled through the redox states of the catalyst or initiator with external stimuli, such as chemical reagents, voltage, or light. However, quick, quantitative, and fully reversible on/off switching of a catalyst still represents a great challenge of temporally controlled polymerization, and stereoselective switch polymerization has been less explored as it is difficult to achieve by the less specific radical or anionic polymerization mechanisms.

Coordination polymerization is a powerful selective process that leads to polymers with superb properties compared to their atactic analogues. However, while coordination polymerization can be easily switched off by external chemical reagents, restarting the polymerization is difficult because of the complexity of the catalytic system. Furthermore, coordination polymerization usually involves chain transfer processes and thus proceeds in a non-living manner. Several elegant approaches have been developed for the polymerization of two active species with tunable monomer selectivity, for example, by means of chain shuttling reagents,[5] degenerative methyl transfer,[6] and ligand oscillation,[7] to create new classes of stereoblock and multiblock copolymers. The only switch on/off coordination polymerization has been realized for norbornene and involved changing the redox state of the ferrocenyl moiety in the phosphine-sulfonate palladium catalyst.[8] The system is non-living, and the switch between the active and dormant species is not quantitative, which hampers the temporal control. Hence, stereo- and temporally controlled coordination polymerization is a promising project but still requires significant development.

Catalysts with a coordinatively unsaturated[9] Lewis acidic metal center easily coordinate THF, pyridine (Py), or other Lewis bases. Coordination of such a Lewis base leads to a dramatic drop in catalytic activity,[10] and their addition is thus usually avoided. On the other hand, a Lewis acidic coactivator such as aluminum or magnesium alkyl compounds could abstract the Lewis base from the metal center to restore the catalytic activity.[11] Herein, we report a strategy for stereo- and temporally controlled switch coordination polymerization. The activity of the catalyst, $[Flu{-}CH_2{-}Py]Y^+(CH_2SiMe_3)$ (**1**), towards isoprene polymerization was switched off and on by alternating addition of Lewis basic pyridine (Py) and Lewis acidic triisobutylaluminum (Al^iBu_3; Scheme 1). The switch is quick, quantitative, and can be repeated multiple times. This system was applied to the copolymerization of isoprene and styrene. In addition, these



Scheme 1. The active and dormant catalyst species **1** and **1**·Py formed upon addition of Al^iBu_3 and pyridine. P = CH_2SiMe_3 or polymer chain.

[*] Dr. B. Liu, Prof. D. M. Cui, Prof. T. Tang
State Key Laboratory of Polymer Physics and Chemistry
Changchun Institute of Applied Chemistry
Chinese Academy of Sciences
No. 5625, Renmin Street, Changchun 130022 (China)
E-mail: dmcui@ciac.ac.cn

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on/off homo- and copolymerizations were performed in living mode and showed high 3,4-selectivity for isoprene polymerization and syndiotactic selectivity for styrene polymerization.

As shown in Figure 1, isoprene (IP) was polymerized for 4 min in the presence of the cationic active species [Flu–CH_2–Py]$Y^+(CH_2SiMe_3)$ (**1**), which was generated in situ by treating the precursor [Flu–CH_2–Py]$Y(CH_2SiMe_3)_2$(THF) with

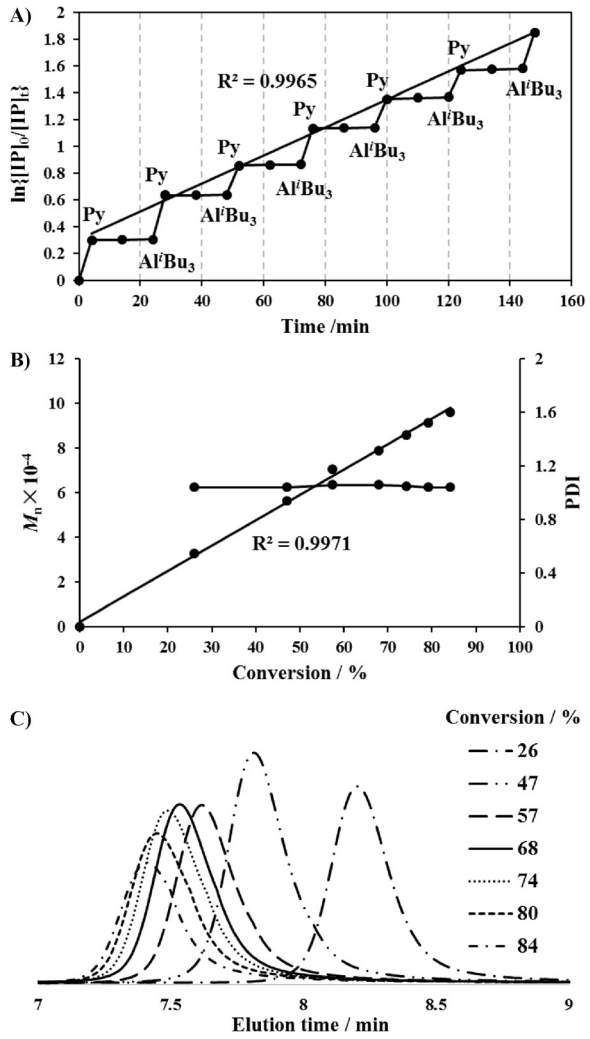

Figure 1. Isoprene polymerization with six cycles of switching between **1** and **1**·Py by addition of pyridine and Al^{i}Bu$_3$. **1** (60 μmol), $[IP]_0/[1]_0 = 1500{:}1$, toluene (70 g), 20 °C. a) ($\ln\{[IP]_0/[IP]_t\}$) as a function of time. B) The molecular weight (M_n) as a function of conversion. C) GPC analysis.

1 equiv $[Ph_3C][B(C_6F_5)_4]$ and then Al^{i}Bu$_3$,[12] which resulted in approximately 26 % conversion (Figure 1 A). The polymerization was living and highly 3,4-selective (> 90 %) with a high rate constant of 30.4 h^{-1} (see the Supporting Information, Figures S1 and S2). Upon pyridine addition, 1:1 complexes of **1** and Lewis basic pyridine (Py) were easily formed (**1**·Py) owing to the Lewis acidic nature and coordinative unsaturation of **1**. Complex **1**·Py was effectively dormant for IP polymerization and about 1500 times less active than **1** (Figure S1), suggesting that the active metal center was poisoned by Py through a Lewis base–acid interaction.[13] Therefore, the IP polymerization ceased immediately upon addition of an equimolar amount of Py, which was confirmed by the color of the solution becoming lighter and the unchanged conversion over 20 min (Figure 1 A, first plateau). For a successful on/off system, it is crucial that the activity of the original catalyst can be recovered promptly and quantitatively. As soon as an equivalent amount of Al^{i}Bu$_3$ (relative to Py) was added, the color of the solution immediately changed from light yellow to dark yellow while the polymerization restarted and reached 47 % total conversion within 4 min (Figure 1 A). These findings indicate that Al^{i}Bu$_3$ successfully abstracted Py from the yttrium center by forming the more stable Al^{i}Bu$_3$·Py adduct to release the original active species **1**. After six cycles of alternating addition of Py and Al^{i}Bu$_3$, the conversion had reached to 84 %.

The semi-logarithmic isoprene conversion versus polymerization time gave a straight line, and the molecular weight increased linearly while the polydispersity was narrow (Figure 1 B, C), demonstrating that the switch between **1** and **1**·Py was rapid, quantitative, and could be repeated multiple times to achieve precise temporal control. The copolymers thus obtained consisted of 3,4-units and were similar to the copolymers obtained by using **1** alone. To the best of our knowledge, we have thus developed the first temporally and stereocontrolled polymerization, which provides high-molecular-weight polymers with turnover numbers up to 1025.[2–4,14]

Intrigued by this exciting result, we attempted a switch on/off copolymerization process, which is more valuable because of the involved sequence control; to the best of our knowledge, such a process has not been reported thus far. To our delight, the copolymerization of IP and styrene (St) catalyzed by **1** was very fast ($k_{app} = 1.98\ h^{-1}$) and proceeded in a living fashion (Figures S3 and S4), whilst that catalyzed by **1**·Py was rather sluggish ($k_{app} = 0.004\ h^{-1}$; Figure S3). Therefore, when the copolymerization of IP and St ($IP/St/Y = 1000{:}1000{:}1$) was performed with **1**·Py, nearly no macromolecules were isolated after 1 h. Addition of Al^{i}Bu$_3$ released **1**, which rapidly catalyzed the copolymerization to reach 20 % conversion within 5 min. After four such circles and 6.5 h, the copolymerization reached complete conversion. The conversion versus time traces indicate the excellent on/off behavior of the copolymerization (Figure S5 A). This was attributed to the rather different activities of **1** and **1**·Py, the rapid, quantitative recovery of **1** from **1**·Py, and the living polymerization mode (Figures S5 B, C). In addition, the isolated copolymers maintained high 3,4-selectivity for the polyisoprene (PIP) units and contained perfect syndiotactic polystyrene (sPS) sequences (Figure S6).[15]

Despite its low activity, **1**·Py could catalyze the living copolymerization ($IP/St/Y = 1000{:}1000{:}1$; Figure S7) to achieve 50 % conversion, albeit over an extended period of time (120 h). Apart from the activity, the differences between catalysts **1** and **1**·Py lie in the reactivity ratios for St and IP monomers. According to the Finemann–Ross equation, the reactivity ratios are $r_{IP} = 42.4$ and $r_{St} = 3.6$ for **1** and $r_{IP} = 6.3$ and $r_{St} = 0.1$ for **1**·Py (Figure S8).[16] Thus the copolymers obtained with **1** have gradient microstructures while those

obtained with **1**·Py have tapered microstructures (Figure 2).[17] We thus conducted a unique sequence-controlled switch copolymerization of IP and St (IP/St/Y = 1000:1000:1) between **1** and **1**·Py where long polymerization times were needed when **1**·Py was the active species

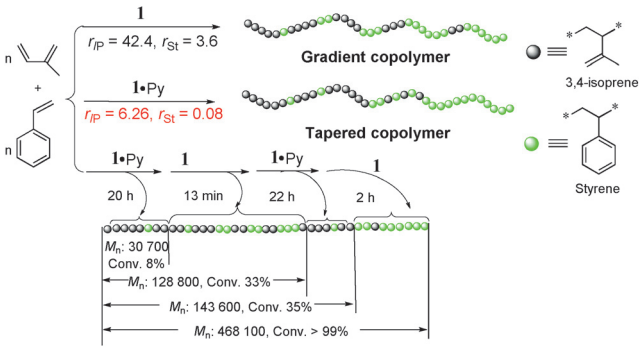

Figure 2. Distribution of the isoprene and styrene units in the copolymers formed upon copolymerization with complexes **1** and **1**·Py and the switch copolymerization with alternating addition of Al^iBu_3 and Py.

(Figure 2). The copolymerization was started with **1**·Py for 20 h to give 8% conversion. The resultant copolymer had long PIP sequences that were separated by discrete St units and a glass transition temperature (T_g) of 31.0 °C, which is close to that of a PIP sample obtained by homopolymerization in the presence of **1**·Py (30.5 °C). Upon addition of Al^iBu_3, the active species was turned into **1**, which immediately speeded up the copolymerization. The monomer conversion reached 33% within 13 min. At this stage, more St units were involved in propagation according to the IP and St reactivity ratios. Correspondingly, the resulting copolymer has a higher T_g (50.3 °C). For the second circle, the copolymerization with **1**·Py was performed for 22 h to reach 35% total conversion, and afforded a copolymer ($M_n = 14.4 \times 10^4$, PDI = 1.1) with a T_g of 42.1 °C. Upon switching back to catalyst **1**, all remaining monomers were completely consumed within 2 h. The obtained copolymer has an increased molecular weight ($M_n = 46.8 \times 10^4$, PDI = 1.2) and a broader T_g range (34.3–80.2 °C), indicating the different sequence distributions (copolymerization with **1** alone: $M_n = 51.8 \times 10^4$, PDI = 1.2, T_g: 38.2–65.6 °C, Figure S9; copolymerization with **1**·Py alone: $M_n = 47.7 \times 10^4$, PDI = 1.2, T_g: 32.9 °C and 90.3 °C).[18]

We further investigated the copolymerization by regulating the switch circles and time intervals between **1** and **1**·Py. As shown in Table 1, for IP/St/Y ratios of 1000:1000:1, no matter how many switch cycles were conducted, all copolymerizations provided copolymers with similar molecular weights ($M_n = 45.0$–47.2×10^4; PDI = 1.2–1.3) at full conversion (> 99%; Table 1). The copolymers A, B, and C, which were obtained at about 30% conversion in the first, second, and third cycle of different experiments, respectively, also have similar molecular weights and narrow molecular weight distributions (A: $M_n = 11.1 \times 10^4$, PDI = 1.1; B: $M_n = 14.4 \times 10^4$, PDI = 1.1; C: $M_n = 14.2 \times 10^4$, PDI = 1.2), but different T_g values (A: 32.3 °C; B: 50.3 °C; C: 60.1 °C) and styrene contents (A: 21 mol%; B: 32 mol%; C: 41 mol%), suggesting different monomer sequences. This was also reflected by their TEM (transmission electron microscopy) images (Figure 3). No micro-phase separation was observed for copolymer A, which is the initial product of the copolymerization catalyzed by **1**·Py, and consists of long PIP sequences separated by discrete styrene units (Figure 3a). For copolymer B, many

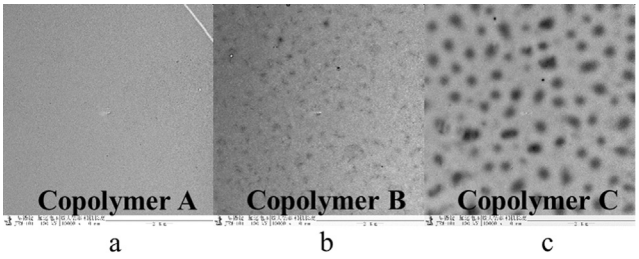

Figure 3. TEM images of copolymers A, B, and C.

small domains were observed that were attributed to the aggregation of continuous sPS sequences generated by the copolymerization with **1** (Figure 3b). For copolymer C, which was isolated after the third circle of the copolymerization, the interval for **1**·Py catalyzed polymerization was short (remembering that **1**·Py was less active than **1**); thus the copolymerization seemed to be controlled by **1**, and more continuous St sequences were incorporated. Therefore, the sPS aggregation domains became larger (Figure 3c). By regulating the switch circles and on/off intervals, different copolymerizations with the same monomer/catalyst ratios and conversions would provide copolymers with similar molecular weights but different monomer sequence distributions, which constitutes a new approach to access tacticity- and sequence-controlled polymers.

In summary, we have reported a new approach for temporally and stereocontrolled coordination polymeri-

Table 1: Switchable copolymerization of isoprene and styrene catalyzed by **1**·Py and **1**.[a]

	One cycle		Two cycles				Three cycles					
	1·Py	**1**	**1**·Py	**1**	**1**·Py	**1**	**1**·Py	**1**	**1**·Py	**1**	**1**·Py	**1**
Time	48 h	2 h	20 h	13 min	22 h	2 h	6 h	6 min	8 h	6 min	8.5 h	2 h
Conv. [%][b]	30	99	8	33	35	99	4	23	24	32	34	99
M_n ($\times 10^4$)[c]	11.1	45.0	3.1	12.9	14.4	46.8	2.3	10.5	11.7	12.4	14.2	47.0
PDI[c]	1.1	1.3	1.1	1.1	1.1	1.2	1.1	1.1	1.1	1.2	1.2	1.2

[a] **1**·Py (81 μmol), IP/St/Y = 1000:1000:1, toluene (28.37 g), 20 °C. [b] Conversion in terms of weight. [c] Determined by high-temperature chromatography.

zation. The activity of the metal catalyst with a Lewis acidic center could be switched off by addition of a Lewis base and switched on upon subsequent addition of a Lewis acidic activator. The switching process is rapid, quantitative, and can be repeated multiple times; not only the catalytic activity but also the selectivity and living character of the polymerization could thus be controlled. The two different catalyst states lead to different reactivity ratios for isoprene and styrene in the copolymerization; adjusting the switch cycles and time intervals of the copolymerization thus leads to copolymers with different compositions and variable monomer-sequence distributions. Hence this temporally and stereocontrolled (co)polymerization constitutes a new approach to mimic natural systems to access tacticity- and sequence-controlled polymers.

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Keywords: coordination polymerization · Lewis acids · Lewis bases · polymerization · sequence-controlled polymers

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