Access to Stereoblock Polyesters via Irreversible Chain-Transfer Ring-Opening Polymerization (ICT-ROP)

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ABSTRACT: Precise control over polymer microstructure can enable molecular tunability of material properties, and stands as a grand challenge in polymer chemistry. Stereoblock copolymers are one of the simplest stereosequenced polymers, yet the synthesis of stereoblock polyesters from prochiral or racemic monomers outside of "simple" isotactic stereoblocks remains limited. Herein, we report the development of irreversible chain-transfer ring-opening polymerization (ICT-ROP), which overcomes fundamental limitations of single catalyst approaches by using transmetallation (e.g., alkoxide-chloride exchange) between two catalysts with distinct stereoselectivities as a means to embed temporally-controlled, multicatalysis in ROP. Our combined small-molecule model and catalytic polymerization studies lay out a clear molecular basis for ICT-ROP, and is exploited to access the first examples of atactic -syndiotactic stereoblock (*at*-sb-*st*) polyesters, *at*-sb-*st* polyhydroxyalkanoates (PHAs). We achieve high levels of control over molecular weight, tacticity, monomer composition, and block structures in a temporally-controlled manner, and demonstrate stereosequence control leads to polymer tensile properties that are independent of thermal properties.

INTRODUCTION

Precise control over polymer microstructure (e.g., composition, sequence, tacticity) can enable unparalleled, molecular tunability of material properties and remains a grand challenge in polymer chemistry.[1] Stereoblock copolymers, sequence-specific materials composed of blocks with differing relative tacticity, are attractive targets, as they can display thermal, mechanical, and degradation properties which are distinct from physical blends of corresponding homopolymers.[2] These materials could be sourced from a single prochiral or racemic monomer pool with the appropriate design of stereospecific catalytic processes. However, this represents a significant fundamental challenge, as a given catalyst-monomer pair typically exhibits a single selectivity. While considerable advances in accessing different stereoblock architectures have been achieved for polyolefins and polyacrylates,[3] access to stereoblock polyesters via ring-opening polymerization (ROP) of a racemic monomer remains limited to "simple" isotactic stereoblocks (alternating runs of isotactic *R*/*S* sequences).[4]

Polyhydroxyalkanoates (PHAs), first discovered nearly 100 years ago,[5] are promising biodegradable materials which can display comparable properties to traditional polyolefins with appropriate control over their composition and microstructure.[6] Recently, Chen and coworkers developed an elegant approach to isotactic-stereoblock-syndiotactic (*it*-sb-*st*) PHAs via the ROP of designer 8-membered diolides using yttrium salen catalysts exhibiting exquisite enantiomorphic site-control (Figure 1A).[6g] The new stereoblock materials displayed improved mechanical and thermal properties compared to their corresponding homopolymers, but required both *rac* and *meso* diastereomers (obtained in low overall yields after multi-step synthesis and purification). Instead, routes to stereoblock PHAs from racemic β-lactones would be highly desirable as they can be sourced in one-step via the catalytic carbonylation of epoxides,[7] yet the generation of stereoblock PHAs from β-lactones remains unknown. Despite the absence of such reports, Coates, Thomas, and coworkers have accessed PHAs with high levels of stereo- and sequence-control (i.e., highly alternating copolymers) via ROP of β-lactones using a syndioselective yttrium salan catalyst exhibiting chain-end stereocontrol.[8] These novel PHAs displayed thermal properties distinct from their corresponding homopolymers, but required the use of *enantiopure* β-lactones (Figure 1B).

Alternatively, straightforward access to stereoblock PHAs should be possible by leveraging catalysts with distinct stereoselectivities in an integrated, multicatalytic approach.[9] While multicatalytic approaches have enabled challenging multi-step organic syntheses,[10] implementing such strategies in ROP would require discrete chain-transfer events. Looking to the synthesis of other stereospecific polyesters, intercatalyst polymeryl exchange has emerged as a distinct pathway for polymer stereo- and sequence-control in ROP, including stereoblocks (Figure 1C).[4a, 11] Although promising, this requires careful management of fast, reversible chain-transfer (k_{ex}) and matched/mismatched rates of propagation (k_p and k_p') to control the properties of the resulting stereoblocks. Chain-transfer agents (CTAs) also induce polymeryl transfer to access block and stereoblock polyesters and polycarbonates,[12] but face similar criteria.

Based on these strategies, we envisioned a modified approach to access stereoblock PHAs from a single racemic

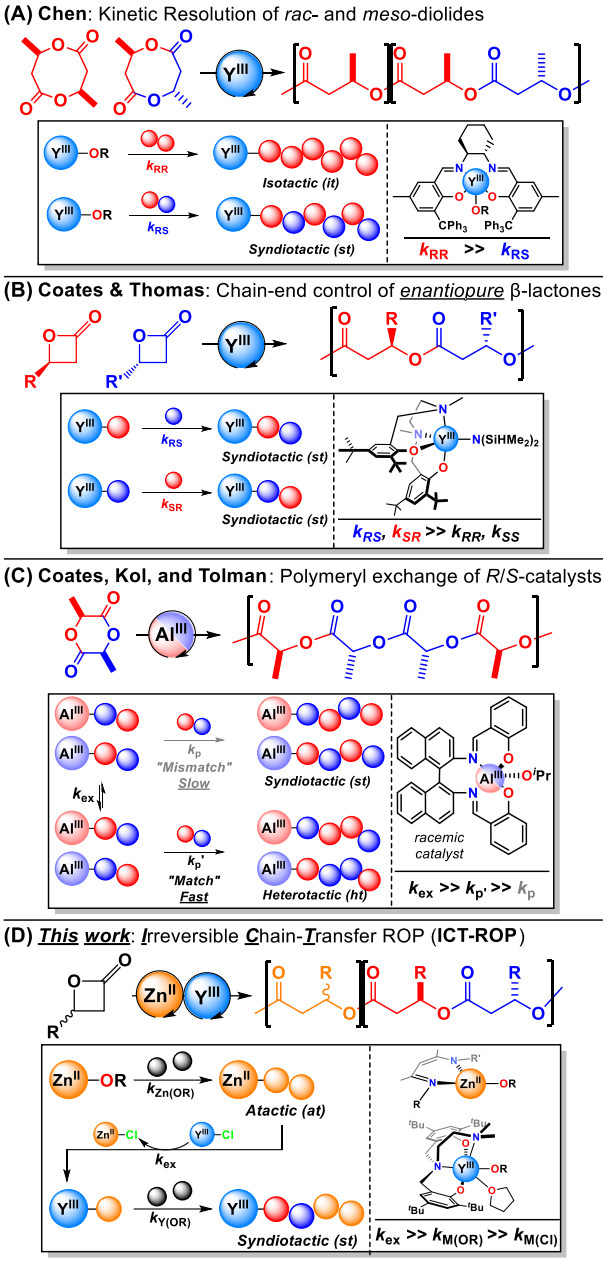


Figure 1. Prior work and mechanistic features driving stereoselectivity to: (A) stereoblock PHA copolymers,[6g] (B) highly-alternating PHA copolymers,[8] and (C) stereoblock polylactide.[4a,11] (D) *This work*: access to stereoblock PHA copolymers from *rac*-β-lactones enable by *I*rreversible *C*hain-*T*ransfer *R*ing-*O*pening *P*olymerization (ICT-ROP).

monomer feed (β-lactones) through a one-time, irreversible polymeryl exchange event (e.g., transmetallation) between catalysts with distinct stereoselectivities via alkoxide-halide exchange (Figure 1D). Unlike degenerate chain-transfer between active and dormant states in coordination chain-transfer polymerization,[13] irreversible polymeryl exchange with an inactive nucleophile (e.g., Cl^-; $k_{M-Cl} << k_{M-OR}$) would enable the temporally-controlled synthesis of stereoblock PHAs. Such a mechanistically-distinct polymerization method might enable access to unknown polyester stereoblock architectures, such as atactic-stereoblock-syndiotactic (*at*-sb-*st*) copolymers. Generally, *at*-sb-*st* copolymers have been challenging to access across all polymer classes,[14] requiring either 1) isolated macroinitiators for each step[15] or 2) fractionation to remove atactic or syndiotactic homopolymers.[16] Herein, we report the development of irreversible chain-transfer ring-opening polymerization (ICT-ROP). ICT-ROP provides access to *at*-sb-*st* PHAs for the first time, and lays the groundwork to access stereo- and sequence-specific polymers using rationally-designed, multicatalytic approaches.

RESULTS & DISCUSSION

In order to realize the envisioned cooperative, multi-catalyst ICT-ROP, two key criteria must be met: (i) facile, irreversible polymeryl (i.e., alkoxide) transfer and (ii) inactivity of the transferred group (i.e., non-alkoxide) towards ROP. With respect to (i), it is well established that transmetallation between organozinc reagents and metal halides,[17] including with group III,[18] is a key elementary step in a diverse range of catalyzed reactions, where the driving force for exchange often follows differences in electronegativity.[19] With respect to (ii), metal halides are typically poor initiators for ROP of lactones, and could serve as the inactive (dormant) state in ICT-ROP. Although zinc alkoxides can react with metal halides to generate heterobimetallic species,[20] quantitative, irreversible alkoxide for chloride exchange is without precedent. With this in mind, we sought to demonstrate the feasibility of these two criteria with two privileged catalyst platforms, zinc beta-diketiminates (BDI)[21] and yttrium aminobisphenolate (OONN'),[22] which can access atactic and syndiotactic poly-3-hydroxybutyrate (P3HB), respectively.

The reaction of 0.5 equiv of Zn Dipp/Bn-substituted beta-diketiminate alkoxide dimer, [Zn(BDI-1)(O^{i}Pr)]$_2$ (**1a-Zn-O^{i}Pr**; generated *in situ* from **1a-Zn-N(SiMe$_3$)$_2$** and ^{i}PrOH,[21b] with one equiv yttrium aminobisphenolate chloride, Y(OONN')(Cl)(THF) (**2-Y-Cl**),[23] was monitored by ^{1}H NMR spectroscopy in d_8-THF (Figure 2A). Over the course of 3 h at RT, **1a-Zn-O^{i}Pr** and **2-Y-Cl** quantitatively and irreversibly formed the anticipated products of alkoxide-chloride exchange, Zn(BDI-1)(Cl)(THF) (**1a-Zn-Cl**) and Y(OONN')(O^{i}Pr)(THF) (**2-Y-O^{i}Pr**) (Figure 2A & 2B). Unambiguous assignment of the products was established through independent syntheses of **1a-Zn-Cl** (Figure 2C, 81% yield) and **2-Y-O^{i}Pr** (Figure S20).[22b] The irreversible nature of the alkoxide-chloride exchange reaction was further confirmed by ^{1}H NMR spectroscopy, where solutions of **1a-Zn-Cl** and **2-Y-O^{i}Pr** remained unchanged at RT after 24 h (Figure S22). Experimental observations were in good agreement with thermochemical predictions obtained from density functional theory (DFT) calculations performed at the M06-L level of theory (Supporting Information, Section 4),[24] with exchange between the hypothetical monomer, **1a'-Zn-O^{i}Pr**, and **2-Y-Cl** favored by 10 kcal/mol (Table S2). Possible chain-transfer processes were probed by 2-dimensional ^{1}H NMR exchange spectroscopy (EXSY) experiments, which revealed negligible rates of exchange between **2-Y-O^{i}Pr** and **2-Y-Cl** or **2-Y-O^{i}Pr** and **1a-Zn-O^{i}Pr** at RT on the NMR time-scale (Figure S25–S28).

Consistent with the limited reactivity of halide,[25] beta-diketiminate,[26] and aminobisphenolate[23] ligands as initiators for the ROP of lactones, both **1a-Zn-Cl** and **2-Y-Cl**, were

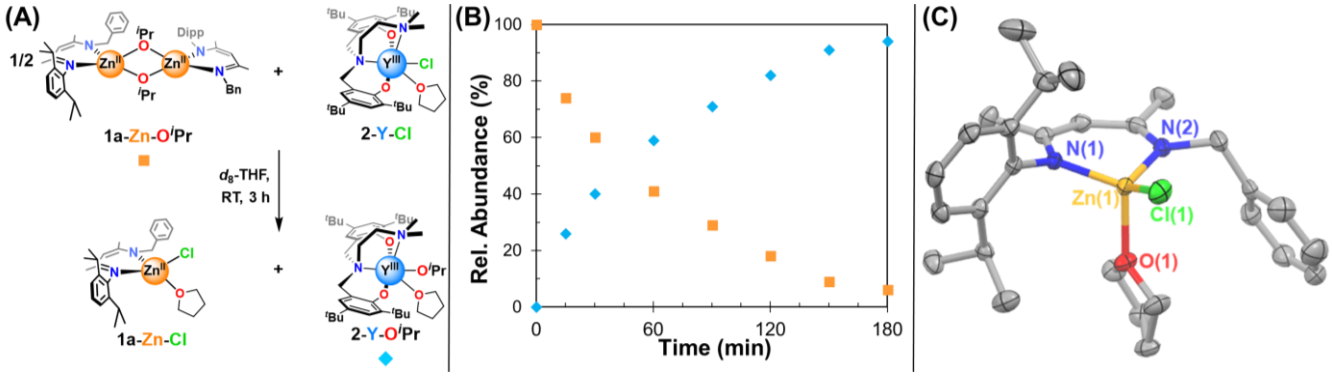
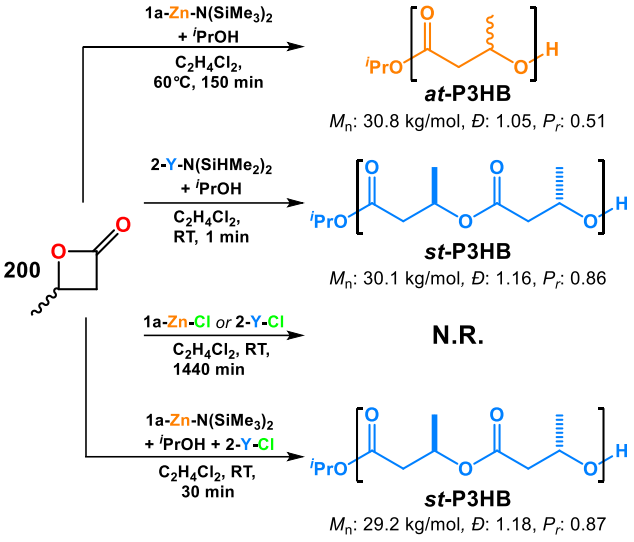


Figure 2. (A) Irreversible alkoxide-chloride exchange between **1a-Zn-O^{i}Pr** and **2-Y-Cl**. (B) Conversion versus time of (A) monitored by ^{1}H NMR spectroscopy. (C) Thermal ellipsoid plot (50% probability) of **1a-Zn-Cl**.



Scheme 1. Homopolymerization controls detailing the reactivity of *rac*-BBL with (i) **1a-Zn-O^{i}Pr**, (ii) **2-Y-O^{i}Pr**, (iii) **2-Y-Cl** or **2-Zn-Cl**, and (iv) **1a-Zn-O^{i}Pr** + **2-Y-Cl**.

inactive for ROP of *rac*-β-butyrolactone (*rac*-BBL) at RT (Scheme 1; Table S12, entries 1 and 2). Under the same conditions, **1a-Zn-O^{i}Pr** and **2-Y-O^{i}Pr** generated atactic- (Scheme 1; *at*-P3HB, P_r = 0.51) and syndiotactic-P3HB (Scheme 1; *st*-P3HB, P_r = 0.86) with narrow molecular weight dispersities (Table S12, entries 3 and 6). Addition of 200 equiv *rac*-BBL to a freshly mixed solution (< 1 min) of **1a-Zn-O^{i}Pr** and **2-Y-Cl** produced *st*-P3HB (Scheme 1; Table 1, entry 1,) with equivalent characteristics as using **2-Y-O^{i}Pr** (Table S12 entry 6) or **2-Y-O^{i}Pr** mixed with **1a-Zn-Cl** (Table 1, entry 2). In sum, our experiments support rapid, irreversible transmetallation between a zinc alkoxide, **1a-Zn-O^{i}Pr**, and yttrium chloride, **2-Y-Cl**, and the resulting yttrium alkoxide is a competent catalyst for the stereospecific ROP of *rac*-BBL.

With both criteria clearly met, we pursued the one-pot synthesis of *at*-sb-*st*-P3HB via ICT-ROP (Figure 3A). In the presence of 200 equiv *rac*-BBL and one equiv isopropanol, **1a-Zn-N(SiMe$_3$)$_2$** reached 47% conversion after 25 min at 60 °C to form narrow dispersity *at*-P3HB (M_n = 14.7 kg/mol, Đ = 1.08, P_r = 0.51; Figure 3B, point 1 and 2). Consistent with the slow reactivity of **1a-Zn-O^{i}Pr** with *rac*-BBL at RT, negligible monomer conversion was observed upon cooling to RT and holding for 35 min (Figure 3B, point 3). ROP commenced rapidly upon addition of **2-Y-Cl** to generate *at*-sb-*st*-P3HB, reaching 96% conversion in ~90 min (Figure 3B, point 4; *at*:*st* = 48:52).

Formation of the desired *at*-sb-*st*-P3HB was unambiguously confirmed by key spectroscopic, chromatographic, and calorimetric techniques. Stereochemical analysis by inverse-gated ^{13}C NMR revealed excellent agreement between experimental ($P_{r,exp}$, 0.71) and theoretical ($P_{r,theo}$, 0.70) tacticity values for the *at*-sb-*st*-P3HB stereoblock copolymer (Supporting Information, Section 5). Size-exclusion chromatography (SEC) revealed a narrow, monomodal molecular weight distribution in good agreement with the predicted molecular weight for a living ROP with a single initiation site (M_n = 32.4 kg/mol, Đ = 1.13). This was in line with rapid, quantitative, and irreversible chain-transfer between the zinc alkoxide propagating chain and **2-Y-Cl** with minimal termination events. 2D ^{1}H NMR diffusion ordered

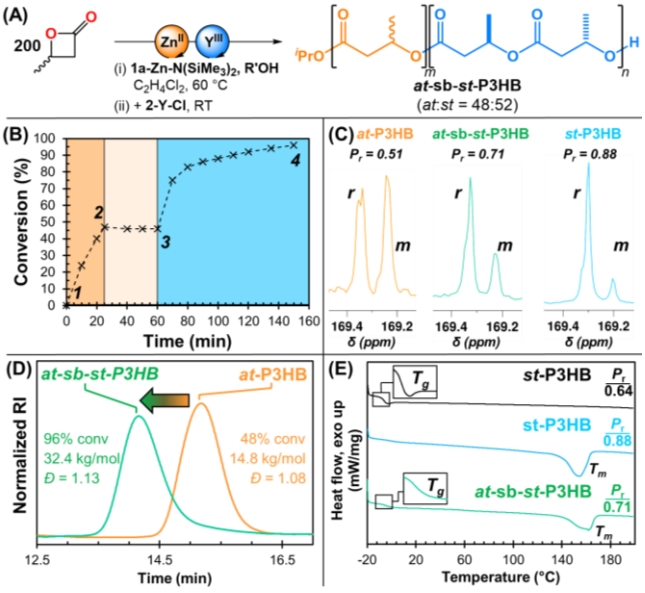


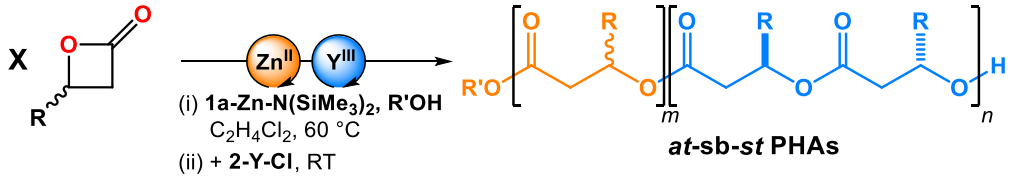
Figure 3. (A) *at*-sb-*st*-P3HB generated from ICT-ROP of *rac*-BBL with **1a-Zn-O^{i}Pr** + **2-Y-Cl**. (B) Conversion of *rac*-BBL versus time of (A): (1) **1a-Zn-O^{i}Pr**, 0%, RT; (2) 48%, 60 °C; (3) 48%, RT; (4) +**2-Y-Cl**, 98%, RT. (C) ^{13}C NMR of the P3HB carbonyl region for *at*-, *at*-sb-*st*-, and *st*-P3HB generated from **1a-Zn-O^{i}Pr**, **1a-Zn-O^{i}Pr** + **2-Y-Cl** (ICT-ROP), and **2-Y-O^{i}Pr**, respectively. (D) SEC traces from points (3) and (4) from panel 3B. (E) Thermal properties of *st*-P3HB (P_r = 0.64), *st*-P3HB (P_r = 0.88), and *at*-sb-*st*-P3HB (P_r = 0.71).

spectroscopy (DOSY) revealed a single diffusion coefficient associated with the copolymer (Figure S36). Finally, differential scanning calorimetry (DSC) revealed distinct thermal properties associated with the novel sequence-specific polymer microstructure (Figure 3E and Table 1, entry 3). Despite being composed of 50% atactic microstructure, *at*-sb-*st*-P3HB (P_r = 0.71) displayed similar melting (T_m) and crystallization (T_c) temperatures to that of the corresponding *st*-P3HB homopolymer, but with lower enthalpies of fusion (ΔH_m, 28 *vs* 42 J/g) and a more pronounced glass transition temperature (T_g). In contrast, thermal analysis of an independently prepared *st*-P3HB homopolymer with more comparable *rac* and *meso* diad content (P_r = 0.64) was completely amorphous (Figure 3E). The disparate thermal behavior of these two samples underscores the dramatic impact of stereosequence control in the resulting polymer properties.

Access to *at*-sb-*st*-P3HB with a range of *at:st* compositions and molecular weights were readily achieved by simply adjusting the timing of **2-Y-Cl** addition and ratio of *rac*-BBL to initiator (i.e., **1a-Zn-O^{i}Pr**), respectively. Addition of **2-Y-Cl** to **1a-Zn-O^{i}Pr**/*rac*-BBL solutions at 74, 48, and 27% conversion (35, 25, and 10 min, respectively) generated increasingly *st*-rich, *at*-sb-*st*-P3HB (*at:st* = 74:26, 48:52, and 27:73), where $P_{r,exp}$ was in excellent agreement with $P_{r,theo}$ (Table 1, entries 4–5). DSC thermal analysis of these samples revealed T_m largely insensitive to *st*-content (Table 1, entries 4–5, 155–161 °C), with a positive linear correlation between ΔH_m and *st*-content (Figure S49 R^2 = 1.00). Polarized light microscopy (PLM) studies performed under isothermal or constant cooling crystallization conditions revealed spherulitic morphologies,[27] where decreased *st*-content led to smaller spherulite size and higher nucleation density (Figure S89 and S90). Maintaining the time of addition of **2-Y-Cl** at ~50% conversion while adjusting the ratio of *rac*-BBL to initiator from 100:1 to 400:1 generated *at*-sb-*st*-P3HB with molecular weights from 14.1–52.4 kg/mol (Table 1, entries 6–7).

Motivated by the high-level tunability of *at*-sb-*st*-P3HB achieved through ICT-ROP with the **1a-Zn-O^{i}Pr/2-Y-Cl** system, we targeted three additional proof-of-concept studies to explore whether we could leverage other catalysts, monomers, and chain-transfer agents. One potential concern is the compatibility of sterically-demanding catalyst partners, as efficient chain-transfer lies at the heart of ICT-ROP. Gratifyingly, employing the more sterically-demanding and higher activity *N*-dibenzhydrylphenyl/*N*-benzyl variant, Zn(BDI-2)[N(SiMe$_3$)$_2$] (**1b-Zn-N(SiMe$_3$)$_2$**),[21b] in place of **1a-Zn-N(SiMe$_3$)$_2$**, generated *at*-sb-*st*-P3HB with excellent control over composition and molecular weight (Table 1, entry 8 and Figure S59–S63). Small alterations in side-chain identity can lead to pronounced effects on PHA thermal properties[28] (R = Me, P3HB: P_r = 0.94, T_m = 178 °C;[29] R = Et, P3HV: P_r = 0.94, T_m = 79 °C).[8] *at*-sb-*st*-P3HV (*at:st* = 52:48) was synthesized via ICT-ROP with **1a-Zn-O^{i}Pr/2-Y-Cl**, which led to a ~100 °C decrease in T_m in comparison to *at*-sb-*st*-P3HB

Table 1. Synthesis of atactic-syndiotactic stereoblock PHA copolymers via ICT-ROP of β-lactones.[a]



Entry	R	X (equiv)	Conv. (%)[b]	[at]:[st][c]	1-Zn-N(SiMe$_3$)$_2$ + R′OH		+ 2-Y-Cl					
					$M_{n,exp}$ (kg/mol)[d]	$Đ$ (M_w/M_n)[d]	$M_{n,exp}$ (kg/mol)[d]	$Đ$ (M_w/M_n)[d]	P_r[c]	T_g (°C)[e]	T_m (°C)[e]	ΔH_m (J/g)[e]
1[f]	Me	200	81	0:100	--	--	30.1	1.16	0.86	--	160	42
2[g]	Me	200	67	0:100	--	--	29.2	1.18	0.87	--	160	42
3	Me	200	96	48:52	14.8	1.08	32.4	1.13	0.71	–2	162	28
4	Me	200	93	27:73	9.9	1.05	31.4	1.13	0.77	2	161	40
5	Me	200	90	74:26	22.9	1.06	29.9	1.10	0.61	–3	155	15
6	Me	100	91	49:51	6.4	1.07	14.1	1.18	0.70	–3	152	15
7	Me	400	90	51:49	31.1	1.04	52.4	1.10	0.68	6	164	33
8[h]	Me	200	96	52:48	17.0	1.05	36.9	1.11	0.69	2	162	30
9	Et	200	92	54:46	14.2	1.06	26.8	1.06	0.65	--	84	24
10[i]	Me	200	93	52:48	15.9	1.07	30.5	1.14	0.67	--	139	16
11[f]	Me	800	94	0:100	--	--	109.0	1.28	0.87	--	159	41
12[h]	Me	800	92	74:26	70.9	1.08	94.2	1.08	0.59	1	156	13
13[h,i]	Me	800	93	70:30	73.9	1.08	92.5	1.09	0.61	1	148	14

a – Unless otherwise noted, reaction conditions are: $C_2H_4Cl_2$ = 1,2-dichloroethane, [β-lactone] = 2.4 M; [β-lactone]:[**1a-Zn-N(SiMe$_3$)$_2$**]:[**2-Y-Cl**]:[R′OH] = X equiv:1:1:1, R′OH = ^{i}PrOH. Reaction times not optimized and see supporting information for reaction times at specific conversions (including **2-Y-Cl** addition points). *b* – Determined by ^{1}H NMR. *c* – Determined by inverse-gated ^{13}C NMR. *d* – Determined by size-exclusion chromatography (SEC), $CHCl_3$ mobile phase. *e* – Determined by differential scanning calorimetry (DSC). *f* – **1a-Zn-N(SiMe$_3$)$_2$**, ^{i}PrOH, and **2-Y-Cl**, followed by adding BBL. Generation of *st*-P3HB homopolymer. *g* – **1a-Zn-Cl**, ^{i}PrOH, and **2-Y-N(SiMe$_3$)$_2$**, followed by adding BBL. Generation of *st*-P3HB homopolymer. *h* –**1b-Zn-N(SiMe$_3$)$_2$** in place of **1a-Zn-N(SiMe$_3$)$_2$**, RT instead of 60 °C. *i* – R′OH = HO(CH$_2$)$_6$OH; formation of *st*-sb-*at*-sb-*st*-P3HB (ABA

(T_m = 80 °C *vs* 162 °C; Table 1, entry 9 *vs* 3 and Figure S64–S69). Multifunctional chain-transfer agents can generate distinct copolymer sequences and/or topologies, which can directly impact polymer properties. Thermoplastic elastomers containing ABA structures (A = hard block, B= soft block) are used in a broad range of applications, and can be readily accessed using bifunctional (telechelic) initiators.[30] Using the bifunctional chain-transfer agent, 1,6-hexanediol, in place of ^{i}PrOH generated the novel ABA triblock, *st*-sb-*at*-sb-*st*-P3HB (Table 1, entry 10 and Figure S70–S75). While *st*-sb-*at*-sb-*st*-P3HB displayed similar thermal properties to the corresponding homopolymer fragments (Table S12, entries 22-23 and Figure S85), PLM studies following isothermal crystallization support formation of much smaller spherulitic domains and signs of microphase separation (Figure S90).[30b, 31]

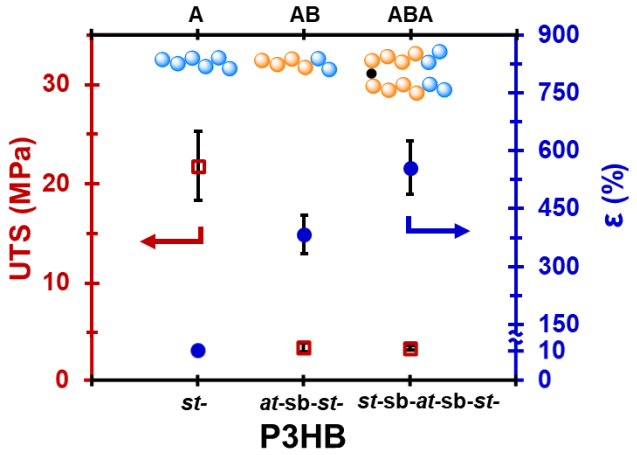


Figure 4. Ultimate tensile strength (UTS) and elongation to break (ε) of *st*-, *at*-sb-*st*- (at:st = 74:26), and *st*-sb-*at*-sb-*st*-P3HB (at:st = 68:32), A, AB, and ABA copolymer structures, respectively (Table 1, entries 11–13; Table S12, entries 20-23).

Tensile testing with dog-bone specimen of high molecular-weight *st*-, *at*-sb-*st*-, and *st*-sb-*at*-sb-*st*-P3HB (≥ 90 kg/mol; *at*:*st* = 0:100, 74:26, 68:72, respectively; Table 1, entries 11–13, see Supporting Information for synthetic details) revealed stereosequence-dependent mechanical properties (Figure 4). While *st*-P3HB was strong but brittle (ultimate tensile-strength, UTS: 21.8 ± 3.5 MPa; elongation-to-break, ε: 10.4 ± 1%), *at*-sb-*st*- (AB) and *st*-sb-*at*-sb-*st*-P3HB (ABA) were weaker with dramatically enhanced ductility (UTS: 3.3 ± 0.4 and 3.2 ± 0.2 MPa and ε: 383 ± 49% and 556 ± 70%, respectively). The improved ductility qualitatively follows expectations based on the decreasing spherulite domain size observed by PLM,[32] where the ~200% increase in ductility moving from AB to ABA architectures underscores the impact of stereosequence control. Alternatively, decomposition (T_d: 246–256 °C) and melting temperatures (T_m: 148–159 °C) were insensitive and independent of tacticity (P_r, *at*:*st* content; Table 1, entries 11–13) or stereoblock architecture (Figures S77-S79, S81-S83, and S85-S87). This stands in stark contrast to the behavior of PHA homopolymers,[6e, f, l, 29, 33] where both thermal and mechanical properties are highly correlated with tacticity. This suggests distinct opportunities to independently tune critical polymer properties solely by stereosequence control, and further connections between structure/morphology and stereoblock copolymer properties are underway.

CONCLUSION

We described the successful development of irreversible chain-transfer ring opening polymerization (ICT-ROP), which we leveraged to access the first examples of atactic-syndiotactic stereoblock polyesters, *at*-sb-*st* PHAs. ICT-ROP overcomes fundamental limitations of the one-catalyst/one-monomer paradigm by using transmetallation (e.g., alkoxide-chloride exchange) between catalysts with distinct stereoselectivities as a means to embed temporally-controlled, multicatalysis in ROP. Our small molecule model studies unambiguously established the irreversible nature of alkoxide-chloride exchange small-molecule, which along with our catalytic polymerization studies laid out a clear molecular basis for ICT-ROP. The highly controlled nature of ICT-ROP allowed for the synthesis of *at*-sb-*st* PHAs with excellent control over molecular weight, tacticity, monomer composition, and block structures, where stereosequence control directly impact polymer properties. We envision ICT-ROP as a powerful method to access other distinct, stereo- and sequence-specific block structures and topologies, and further studies are currently underway.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.
Detailed materials and methods including synthetic details, characterization, and computational methods.

Accession Codes
CCDC 2266984 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a)Celebrating 50 Years of Macromolecules. *Macromolecules* **2017,** *50*, 9525-9527; (b)Bates, F. S.; Hillmyer, M. A.; Lodge, T. P.; Bates, C. M.; Delaney, K. T.; Fredrickson, G. H., Multiblock Polymers: Panacea or Pandora's Box? *Science* **2012,** *336*, 434-440; (c)Lutz, J.-F.; Ouchi, M.; Liu, D. R.; Sawamoto, M., Sequence-Controlled Polymers. *Science* **2013,** *341*, 1238149.

(2) (a)Natta, G., Properties of isotactic, atactic, and stereoblock homopolymers, random and block copolymers of α-olefins. *J. Polym. Sci.* **1959,** *34*, 531-549; (b)Collette, J. W.; Tullock, C. W.; MacDonald, R. N.; Buck, W. H.; Su, A. C. L.; Harrell, J. R.; Mulhaupt, R.; Anderson, B. C., Elastomeric polypropylenes from alumina-supported tetraalkyl Group IVB catalysts. 1. Synthesis and properties of high molecular weight stereoblock homopolymers. *Macromolecules* **1989,** *22*, 3851-3858; (c)Rosen, T.; Goldberg, I.; Navarra, W.; Venditto, V.; Kol, M., Block–Stereoblock Copolymers of Poly(ϵ-Caprolactone) and Poly(Lactic Acid). *Angew. Chem. Int. Ed.* **2018,** *57*, 7191-7195; (d)Hietala, S.; Nuopponen, M.; Kalliomäki, K.; Tenhu, H., Thermoassociating Poly(N-isopropylacrylamide) A–B–A Stereoblock Copolymers. *Macromolecules* **2008,** *41*, 2627-2631.

(3) (a)Coates, G. W.; Waymouth, R. M., Oscillating Stereocontrol: A Strategy for the Synthesis of Thermoplastic Elastomeric Polypropylene. *Science* **1995,** *267*, 217-219; (b)Hatada, K., Stereoregular uniform polymers. *J. Polym. Sci., Part A: Polym. Chem.* **1999,** *37*, 245-260; (c)Suhm, J.; Heinemann, J.; Wörner, C.; Müller, P.; Stricker, F.; Kressler, J.; Okuda, J.; Mülhaupt, R., Novel polyolefin materials via catalysis and reactive processing. *Macromol. Symp.* **1998,** *129*, 1-28; (d)Bolig, A. D.; Chen, E. Y. X., Isotactic-b-Syndiotactic Stereoblock Poly(methyl methacrylate) by Chiral Metallocene/Lewis Acid Hybrid Catalysts. *J. Am. Chem. Soc.* **2002,** *124*, 5612-5613; (e)Lutz, J.-F.; Neugebauer, D.; Matyjaszewski, K., Stereoblock Copolymers and Tacticity Control in Controlled/Living Radical Polymerization. *J. Am. Chem. Soc.* **2003,** *125*, 6986-6993; (f)Kamigaito, M.; Satoh, K., Stereoregulation in Living Radical Polymerization. *Macromolecules* **2008,** *41*, 269-276.

(4) (a)Ovitt, T. M.; Coates, G. W., Stereochemistry of Lactide Polymerization with Chiral Catalysts: New Opportunities for Stereocontrol Using Polymer Exchange Mechanisms. *J. Am. Chem. Soc.* **2002,** *124*, 1316-1326; (b)Abbina, S.; Du, G., Zinc-Catalyzed Highly Isoselective Ring Opening Polymerization of rac-Lactide. *ACS Macro Lett.* **2014,** *3*, 689-692; (c)Myers, D.; White, A. J. P.; Forsyth, C. M.; Bown, M.; Williams, C. K., Phosphasalen Indium Complexes Showing High Rates and Isoselectivities in rac-Lactide Polymerizations. *Angew. Chem. Int. Ed.* **2017,** *56*, 5277-5282; (d)Stopper, A.; Rosen, T.; Venditto, V.; Goldberg, I.; Kol, M., Group 4 Metal Complexes of Phenylene–Salalen Ligands in rac-Lactide Polymerization Giving High Molecular Weight Stereoblock Poly(lactic acid). *Chem. Eur. J.* **2017,** *23*, 11540-11548; (e)Hu, J.; Kan, C.; Ma, H., Exploring Steric Effects of Zinc Complexes Bearing Achiral Benzoxazolyl Aminophenolate Ligands in Isoselective Polymerization of rac-Lactide. *Inorg. Chem.* **2018,** *57*, 11240-11251; (f)Liu, Y.; Zhang, J.; Kou, X.; Liu, S.; Li, Z., Highly Active Organocatalysts for Stereoselective Ring-Opening Polymerization of Racemic Lactide at Room Temperature. *ACS Macro Lett.* **2022,** *11*, 1183-1189.

(5) (a)Lemoigne, M., de l'acide 3-oxybutyrique. *Bull Soc Chim Biol (Paris)* **1926,** *8*, 770; (b)Marchessault, R. H.; Debzi, E. M.; Revol, J. F.; Steinbuechel, A., Single crystals of bacterial and synthetic poly(3-hydroxyvalerate). *Can. J. Microbiol.* **1995,** *41*, 297-302.

(6) (a)Rieger, B.; Künkel, A.; Coates, G. W.; Reichardt, R.; Dinjus, E.; Zevaco, T. A., Synthetic Biodegradable Polymers. Springer Berlin: Berlin, 2014; pp 49-90; (b)Westlie, A. H.; Quinn, E. C.; Parker, C. R.; Chen, E. Y. X., Synthetic biodegradable polyhydroxyalkanoates (PHAs): Recent advances and future challenges. *Prog. Polym. Sci.* **2022,** *134*, 101608; (c)Bugnicourt, E.; Cinelli, P.; Lazzeri, A.; Alvarez, V., Polyhydroxyalkanoate (PHA): Review of synthesis, characteristics, processing and potential applications in packaging. *EXPRESS Polym. Lett.* **2014,** *8*, 791-808; (d)Raza, Z. A.; Abid, S.; Banat, I. M., Polyhydroxyalkanoates: Characteristics, production, recent developments and applications. *Int. Biodeterior. Biodegradation* **2018,** *126*, 45-56; (e)Abe, H.; Matsubara, I.; Doi, Y.; Hori, Y.; Yamaguchi, A., Physical Properties and Enzymic Degradability of Poly(3-hydroxybutyrate) Stereoisomers with Different Stereoregularities. *Macromolecules* **1994,** *27*, 6018-6025; (f)Haslböck, M.; Klotz, M.; Sperl, J.; Sieber, V.; Zollfrank, C.; Van Opdenbosch, D., Mechanical and Thermal Properties of Mixed-Tacticity Polyhydroxybutyrates and Their Association with Iso- and Atactic Chain Segment Length Distributions. *Macromolecules* **2019,** *52*, 5407-5418; (g)Tang, X.; Westlie, A. H.; Watson, E. M.; Chen, E. Y.-X., Stereosequenced crystalline polyhydroxyalkanoates from diastereomeric monomer mixtures. *Science* **2019,** *366*, 754-758; (h)Dong, X.; Robinson, J. R., The role of neutral donor ligands in the isoselective ring-opening polymerization of rac-β-butyrolactone. *Chem. Sci.* **2020,** *11*, 8184-8195; (i)Zhou, Z.; LaPointe, A. M.; Shaffer, T. D.; Coates, G. W., Nature-inspired methylated polyhydroxybutyrates from C1 and C4 feedstocks. *Nat. Chem.* **2023,** *15*, 856-861; (j)Zhou, L.; Zhang, Z.; Shi, C.; Scoti, M.; Barange, D. K.; Gowda, R. R.; Chen, E. Y.-X., Chemically circular, mechanically tough, and melt-processable polyhydroxyalkanoates. *Science* **2023,** *380*, 64-69; (k)Bruckmoser, J.; Pongratz, S.; Stieglitz, L.; Rieger, B., Highly Isoselective Ring-Opening Polymerization of rac-β-Butyrolactone: Access to Synthetic Poly(3-hydroxybutyrate) with Polyolefin-like Material Properties. *J. Am. Chem. Soc.* **2023,** *145*, 11494-11498; (l)Huang, H.-Y.; Xiong, W.; Huang, Y.-T.; Li, K.; Cai, Z.; Zhu, J.-B., Spiro-salen catalysts enable the chemical synthesis of stereoregular polyhydroxyalkanoates. *Nat. Catal.* **2023,** *6*, 720-728.

(7) (a)Getzler, Y. D. Y. L.; Mahadevan, V.; Lobkovsky, E. B.; Coates, G. W., Synthesis of β-Lactones: A Highly Active and Selective Catalyst for Epoxide Carbonylation. *J. Am. Chem. Soc.* **2002,** *124*, 1174-1175; (b)Molnar, F.; Luinstra, G. A.; Allmendinger, M.; Rieger, B., Multisite Catalysis: A Mechanistic Study of β-Lactone Synthesis from Epoxides and CO—Insights into a Difficult Case of Homogeneous Catalysis. *Chem. Eur. J.* **2003,** *9*, 1273-1280; (c)Kramer, J. W.; Lobkovsky, E. B.; Coates, G. W., Practical β-Lactone Synthesis: Epoxide Carbonylation at 1 atm. *Org. Lett.* **2006,** *8*, 3709-3712.

(8) Kramer, J. W.; Treitler, D. S.; Dunn, E. W.; Castro, P. M.; Roisnel, T.; Thomas, C. M.; Coates, G. W., Polymerization of Enantiopure Monomers Using Syndiospecific Catalysts: A New Approach To Sequence Control in Polymer Synthesis. *J. Am. Chem. Soc.* **2009,** *131*, 16042-16044.

(9) Deng, S.; Jolly, B. J.; Wilkes, J. R.; Mu, Y.; Byers, J. A.; Do, L. H.; Miller, A. J. M.; Wang, D.; Liu, C.; Diaconescu, P. L., Spatiotemporal control for integrated catalysis. *Nat. Rev. Methods Primers* **2023,** *3*, 28.

(10) (a)Sancheti, S. P.; Urvashi; Shah, M. P.; Patil, N. T., Ternary Catalysis: A Stepping Stone toward Multicatalysis. *ACS Catal.* **2020,** *10*, 3462-3489; (b)Martínez, S.; Veth, L.; Lainer, B.; Dydio, P., Challenges and Opportunities in Multicatalysis. *ACS Catal.* **2021,** *11*, 3891-3915.

(11) (a)Press, K.; Goldberg, I.; Kol, M., Mechanistic Insight into the Stereochemical Control of Lactide Polymerization by Salan–Aluminum Catalysts. *Angew. Chem. Int. Ed.* **2015,** *54*, 14858-14861; (b)Hador, R.; Botta, A.; Venditto, V.; Lipstman, S.; Goldberg, I.; Kol, M., The Dual-Stereocontrol Mechanism: Heteroselective Polymerization of rac-Lactide and Syndioselective Polymerization of meso-Lactide by Chiral Aluminum Salan Catalysts. *Angew. Chem. Int. Ed.* **2019,** *58*, 14679-14685; (c)Peterson, A.; Hador, R.; Pink, M.; Popowski, Y.; Kol, M.; Tolman, W. B., Defining Stereochemistry in the Polymerization of Lactide by Aluminum Catalysts: Insights into the Dual-Stereocontrol Mechanism. *J. Am. Chem. Soc.* **2022,** *144*, 20047-20055.

(12) (a)Liu, Y.; Ren, W.-M.; Zhang, W.-P.; Zhao, R.-R.; Lu, X.-B., Crystalline CO2-based polycarbonates prepared from racemic catalyst through intramolecularly interlocked assembly. *Nat. Commun.* **2015,** *6*, 8594; (b)Childers, M. I.; Vitek, A. K.; Morris, L. S.; Widger, P. C. B.; Ahmed, S. M.; Zimmerman, P. M.; Coates, G. W., Isospecific, Chain Shuttling Polymerization of Propylene Oxide Using a Bimetallic Chromium Catalyst: A New Route to Semicrystalline Polyols. *J. Am. Chem. Soc.* **2017,** *139*, 11048-11054; (c)Clayman, N. E.; Morris, L. S.; LaPointe, A. M.; Keresztes, I.; Waymouth, R. M.; Coates, G. W., Dual catalysis for the copolymerisation of epoxides and lactones. *Chemical Commun.* **2019,** *55*, 6914-6917; (d)Meimoun, J.; Sutapin, C.; Stoclet, G.; Favrelle, A.; Roussel, P.; Bria, M.; Chirachanchai, S.; Bonnet, F.; Zinck,

P., Lactide Lactone Chain Shuttling Copolymerization Mediated by an Aminobisphenolate Supported Aluminum Complex and Al(OiPr)3: Access to New Polylactide Based Block Copolymers. *J. Am. Chem. Soc.* **2021,** *143*, 21206-21210.
(13) (a)Jayaratne, K. C.; Sita, L. R., Direct Methyl Group Exchange between Cationic Zirconium Ziegler−Natta Initiators and Their Living Polymers: Ramifications for the Production of Stereoblock Polyolefins. *J. Am. Chem. Soc.* **2001,** *123*, 10754-10755; (b)Zhang, Y.; Sita, L. R., Stereospecific Living Ziegler−Natta Polymerization via Rapid and Reversible Chloride Degenerative Transfer between Active and Dormant Sites. *J. Am. Chem. Soc.* **2004,** *126*, 7776-7777; (c)Kamigaito, M.; Satoh, K.; Uchiyama, M., Degenerative chain-transfer process: Controlling all chain-growth polymerizations and enabling novel monomer sequences. *J. Polym. Sci., Part A: Polym. Chem.* **2019,** *57*, 243-254.
(14) (a)Nishii, K.; Shiono, T.; Ikeda, T., A Novel Synthetic Procedure for Stereoblock Poly(propylene) with a Living Polymerization System. *Macromol. Rapid Commun.* **2004,** *25*, 1029-1032; (b)Cai, Z.; Nakayama, Y.; Shiono, T., Synthesis of crystallizable sydiotactic-atactic stereoblock polypropylene using a living polymerization system. *Kinetics and Catalysis* **2006,** *47*, 274-277; (c)Tao, Y.; Satoh, K.; Kamigaito, M., Nucleobase-Mediated Stereospecific Radical Polymerization and Combination with RAFT Polymerization for Simultaneous Control of Molecular Weight and Tacticity. *Macromol. Rapid Commun.* **2011,** *32*, 226-232.
(15) (a)Shibata, T.; Satoh, K.; Kamigaito, M.; Okamoto, Y., Simultaneous control of the stereospecificity and molecular weight in the ruthenium-catalyzed living radical polymerization of methyl and 2-hydroxyethyl methacrylates and sequential synthesis of stereoblock polymers. *J. Polym. Sci., Part A: Polym. Chem.* **2006,** *44*, 3609-3615; (b)Annunziata, L.; Sarazin, Y.; Duc, M.; Carpentier, J.-F., Well-defined Syndiotactic Polystyrene-b-Atactic Polystyrene Stereoblock Polymers. *Macromol. Rapid Commun.* **2011,** *32*, 751-757; (c)Ishitake, K.; Satoh, K.; Kamigaito, M.; Okamoto, Y., Stereospecific Free Radical and RAFT Polymerization of Bulky Silyl Methacrylates for Tacticity and Molecular Weight Controlled Poly(methacrylic acid). *Macromolecules* **2011,** *44*, 9108-9117.
(16) (a)Jin, J.; Chen, E. Y.-X., Stereoblock Copolymerization of Propylene and Methyl Methacrylate with Single-Site Metallocene Catalysts. *Macromol. Chem. Phys.* **2002,** *203*, 2329-2333; (b)Chen, R.; Wu, Q.; Zhu, F.; Lin, S., Syndiotactic polystyrene-b-atactic polypropylene block copolymer alloy as a compatibilizer for syndiotactic polystyrene/isotactic polypropylene blends. *J. Appl. Polym. Sci.* **2003,** *89*, 1596-1605; (c)Longo, P.; Mariconda, A.; D'Urso, L.; Napoli, M., Syndiotactic–Atactic Stereoblock Polystyrene Obtained with a Hapto-Flexible Catalyst. *Macromolecules* **2014,** *47*, 2214-2218.
(17) (a)Knochel, P.; Singer, R. D., Preparation and reactions of polyfunctional organozinc reagents in organic synthesis. *Chem. Rev.* **1993,** *93*, 2117-2188; (b)Choi, J.; Fu, G. C., Transition metal–catalyzed alkyl-alkyl bond formation: Another dimension in cross-coupling chemistry. *Science* **2017,** *356*, eaaf7230.
(18) (a)Belli, R. G.; Tafuri, V. C.; Joannou, M. V.; Roberts, C. C., d0 Metal-Catalyzed Alkyl–Alkyl Cross-Coupling Enabled by a Redox-Active Ligand. *ACS Catal.* **2022,** *12*, 3094-3099; (b)Gavin, J. T.; Belli, R. G.; Roberts, C. C., Radical-Polar Crossover Catalysis with a d0 Metal Enabled by a Redox-Active Ligand. *J. Am. Chem. Soc.* **2022,** *144*, 21431-21436.
(19) Hartwig, J. F., *Organotransition metal chemistry: from bonding to catalysis*. University Science Books: Sausalito, California, 2010.
(20) (a)Yonemura, M.; Usuki, N.; Nakamura, Y.; Ohba, M.; Ōkawa, H., Macrocyclic effect upon site-selective CuIIMII or MIICuII core formation with unsymmetric phenol-based macrocyclic ligands. *Dalton Trans.* **2000**, 3624-3631; (b)Feng, W.-X.; Hui, Y.-N.; Shi, G.-X.; Zou, D.; Lü, X.-Q.; Song, J.-R.; Fan, D.-D.; Wong, W.-K.; Jones, R. A., Synthesis, structure and near-infrared (NIR) luminescence of series of Zn2Ln (Ln=Nd, Yb or Er) complexes based on the Salen-type Schiff-base ligand with the flexible linker. *Inorg. Chem. Commun.* **2012,** *20*, 33-36.
(21) (a)Rieth, L. R.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W., Single-Site β-Diiminate Zinc Catalysts for the Ring-Opening Polymerization of β-Butyrolactone and β-Valerolactone to Poly(3-hydroxyalkanoates). *J. Am. Chem. Soc.* **2002,** *124*, 15239-15248; (b)Chellali, J. E.; Alverson, A. K.; Robinson, J. R., Zinc Aryl/Alkyl β-diketiminates: Balancing Accessibility and Stability for High-Activity Ring-Opening Polymerization of rac-Lactide. *ACS Catal.* **2022,** *12*, 5585-5594.
(22) (a)Amgoune, A.; Thomas, C. M.; Ilinca, S.; Roisnel, T.; Carpentier, J.-F., Highly Active, Productive, and Syndiospecific Yttrium Initiators for the Polymerization of Racemic β-Butyrolactone. *Angew. Chem. Int. Ed.* **2006,** *45*, 2782-2784; (b)Nie, K.; Fang, L.; Yao, Y.; Zhang, Y.; Shen, Q.; Wang, Y., Synthesis and Characterization of Amine-Bridged Bis(phenolate)lanthanide Alkoxides and Their Application in the Controlled Polymerization of rac-Lactide and rac-β-Butyrolactone. *Inorg. Chem.* **2012,** *51*, 11133-11143; (c)Carpentier, J.-F., Rare-Earth Complexes Supported by Tripodal Tetradentate Bis(phenolate) Ligands: A Privileged Class of Catalysts for Ring-Opening Polymerization of Cyclic Esters. *Organometallics* **2015,** *34*, 4175-4189.
(23) Willans, C. E.; Sinenkov, M. A.; Fukin, G. K.; Sheridan, K.; Lynam, J. M.; Trifonov, A. A.; Kerton, F. M., Lanthanide chloride complexes of amine-bis(phenolate) ligands and their reactivity in the ring-opening polymerization of ε-caprolactone. *Dalton Trans.* **2008**, 3592-3598.
(24) Zhao, Y.; Truhlar, D. G., A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. *J. Chem. Phys.* **2006,** *125*.
(25) (a)Yasuda, T.; Aida, T.; Inoue, S., Living polymerization of .beta.-lactone catalyzed by (tetraphenylporphinate)aluminum chloride. Structure of the living end. *Macromolecules* **1983,** *16*, 1792-1796; (b)Vagin, S.; Winnacker, M.; Kronast, A.; Altenbuchner, P. T.; Deglmann, P.; Sinkel, C.; Loos, R.; Rieger, B., New Insights into the Ring-Opening Polymerization of β-Butyrolactone Catalyzed by Chromium(III) Salphen Complexes. *ChemCatChem* **2015,** *7*, 3963-3971.
(26) Xue, M.; Jiao, R.; Zhang, Y.; Yao, Y.; Shen, Q., Syntheses and Structures of Tris-β-Diketiminate Lanthanide Complexes and Their High Activity for Ring-Opening Polymerization of ϵ-Caprolactone and L-Lactide. *Eur. J. Inorg. Chem.* **2009,** *2009*, 4110-4118.
(27) (a)Abe, H.; Doi, Y., Molecular and Material Design of Biodegradable Poly(hydroxyalkanoate)s. In *Polyesters II: Properties and Chemical Synthesis*, Steinbüchel, A.; Doi, Y., Eds. Wiley-Blackwell: 2002; Vol. 3b, pp 105-132; (b)Caputo, M. R.; Tang, X.; Westlie, A. H.; Sardon, H.; Chen, E. Y. X.; Müller, A. J., Effect of Chain Stereoconfiguration on Poly(3-hydroxybutyrate) Crystallization Kinetics. *Biomacromolecules* **2022,** *23*, 3847-3859.
(28) (a)*Polyesters II: Properties and Chemical Synthesis*. John Wiley & Sons, Ltd: Chichester, UK, 2003; Vol. 52; (b)Rieger, B. K., A.; Coates, G. W.; Reichardt, R.; Dinjus, E.; Zevaco, T. A., *Synthetic Biodegradable Polymers*. 1 ed.; Springer Berlin, Heidelberg: 2012; p XIV, 366.
(29) Ajellal, N.; Bouyahyi, M.; Amgoune, A.; Thomas, C. M.; Bondon, A.; Pillin, I.; Grohens, Y.; Carpentier, J.-F., Syndiotactic-Enriched Poly(3-hydroxybutyrate)s via Stereoselective Ring-Opening Polymerization of Racemic β-Butyrolactone with Discrete Yttrium Catalysts. *Macromolecules* **2009,** *42*, 987-993.
(30) (a)Holden, G., *Understanding thermoplastic elastomers*. Hanser: Cincinnati, 2000; (b)Hillmyer, M. A.; Tolman, W. B., Aliphatic Polyester Block Polymers: Renewable, Degradable, and Sustainable. *Acc. Chem. Res.* **2014,** *47*, 2390-2396; (c)Wang, W.; Lu, W.; Goodwin, A.; Wang, H.; Yin, P.; Kang, N.-G.; Hong, K.; Mays, J. W., Recent advances in thermoplastic elastomers from living polymerizations: Macromolecular architectures and supramolecular chemistry. *Prog. Polym. Sci.* **2019,** *95*, 1-31.
(31) (a)MacDonald, J. P.; Parker, M. P.; Greenland, B. W.; Hermida-Merino, D.; Hamley, I. W.; Shaver, M. P., Tuning thermal properties and microphase separation in aliphatic polyester ABA copolymers. *Polym. Chem.* **2015,** *6*, 1445-1453; (b)Quinn, E. C.; Westlie, A. H.; Sangroniz, A.; Caputo, M. R.; Xu, S.; Zhang, Z.; Urgun-Demirtas, M.; Müller, A. J.; Chen, E. Y. X., Installing Controlled Stereo-Defects Yields Semicrystalline and Biodegradable Poly(3-Hydroxybutyrate) with High Toughness and Optical Clarity. *J. Am. Chem. Soc.* **2023,** *145*, 5795-5802.
(32) Pietrangelo, A.; López-Barrón, C. R.; DeRocco, M. T.; Kang, S.; Mattler, S. J.; Wright, P. J., Tuning the Morphology, Thermal Behavior, and Toughness of Poly(β-butyrolactone-co-β-valerolactone) Thermoplastics. *Macromolecules* **2023,** *56*, 5588-5598.

(33) Kricheldorf, H. R.; Eggerstedt, S., Polylactones. 41. Polymerizations of β-d,l-Butyrolactone with Dialkyltinoxides as Initiators. *Macromolecules* **1997,** *30,* 5693-5697.