ABCD Block Copolymers Using a Multistate Aluminum Complex

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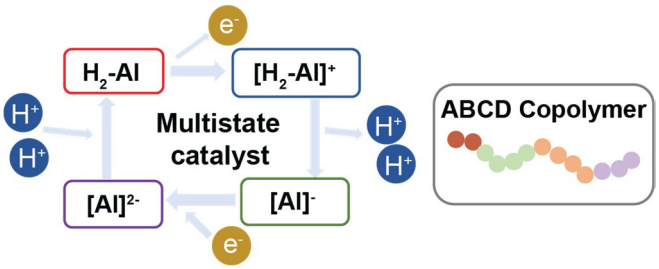
KEYWORDS Copolymerization, biodegradable copolymers, monomers, redox switch, protonation switch

ABSTRACT: A ferrocene aluminum compound (salfan-H_2)Al(OiPr) (salfan-H_2 = 1,1'-di(2,4-bis-*tert*-butyl-salicylamino)ferrocene), with adjustable redox and protonation characteristics, has been synthesized and characterized, and serves as a switchable catalyst for ring-opening polymerization. Leveraging this versatile, multistate system, we have successfully synthesized a range of innovative copolymers, including AB diblock poly(styrene oxide-lactide) (PSO-PLA), ABC triblock poly(butyl lactone-styrene oxide-lactide) (PBBL-PSO-PLA), and ABCD tetrablock copolymers poly(ethoxy vinyl glycidyl ether-butyl lactone-styrene oxide-lactide) (PEVGE-PBBL-PSO-PLA).



Introduction

Multiblock copolymers with diverse monomer units result in a distinctive polymeric architecture and microstructure that imparts unique properties not found in the corresponding homopolymers.[1-8] Despite great achievements in the last decade, only few examples of multiblock copolymers composed of more than three different blocks were reported by using ring opening copolymerization.[9-17] For example, in 2018, Williams and coworkers reported the utilization of a dizinc catalyst for the one-pot synthesis of a pentablock copolymer composed of four distinct components, including anhydride, epoxide, lactone, and CO_2.[18] In 2021, Chen and coworkers reported a salen-Mn(III) catalyst capable of constructing a seven-block copolymer with three distinct monomer units.[19] In 2023, Satoh and coworkers accomplished the synthesis of a heptablock copolymer comprised of cyclic anhydrides, cyclic esters, and epoxides, all within a single reaction vessel, with five distinct monomer units.[20]

Switchable polymerization catalysts have distinct active states and selectivity for various monomers, and, therefore, can be employed to achieve controlled formation of multiblock copolymers.[14, 21-30] Over the past decade, our strategy has involved harnessing metal complexes with ligands derived from ferrocene to achieve unique reactivity, enabling chemical or electrochemical control over the redox states in the metal complex.[31-49] This unique property facilitates the synthesis of block copolymers with a high degree of control. In 2021, we reported electrochemical control using a ferrocene zirconium complex to develop an ABC triblock and an ABAB tetrablock copolymer.[50]

Most switchable catalysts exist as a two-state system, i.e., the metal complex is catalytically active in only two forms; in redox switchable catalysis, these two forms are the reduced and oxidized state of the system.[51-59] In 2016, Chen and coworkers reported an α-diimine palladium compound, Pd-CN (Chart 1), which was the first example of a catalytic system that was amenable to two stepwise oxidations.[60] The three oxidation states not only had different catalytic activities toward ethylene polymerization but also produced polyethylene with different molar masses and different topologies. Another example was reported by Hey-Hawkins and coworkers, who showed that a trinuclear gold(I) complex supported by a tris(ferrocenyl)arene-based tris-phosphine, $[Au]_3$, had four accessible oxidation states, making it possible to tune in a stepwise fashion the rate of catalytic ring-closing isomerisation of *N*-(2-propyn-1-yl)benzamide.[61] In 2021, we developed a three-state dimeric yttrium phenoxide complex supported by a ferrocene Schiff base ligand. However, it was unsuccessful in forming an ABC triblock copolymer (Figure 1a). To the best of our knowledge, a system with multiple states has not been successful in the formation of multiblock copolymers using the ring opening polymerization of cyclic esters and ethers.

Herein, we report a novel ferrocene aluminum complex with distinct orthogonal reactivity, exhibiting both redox and protonation control (Figure 1b), and enabling the formation of ABC and ABCD block copolymers. This represents the first application of orthogonal chemical switches in crafting a tetrablock copolymer containing four distinct units.

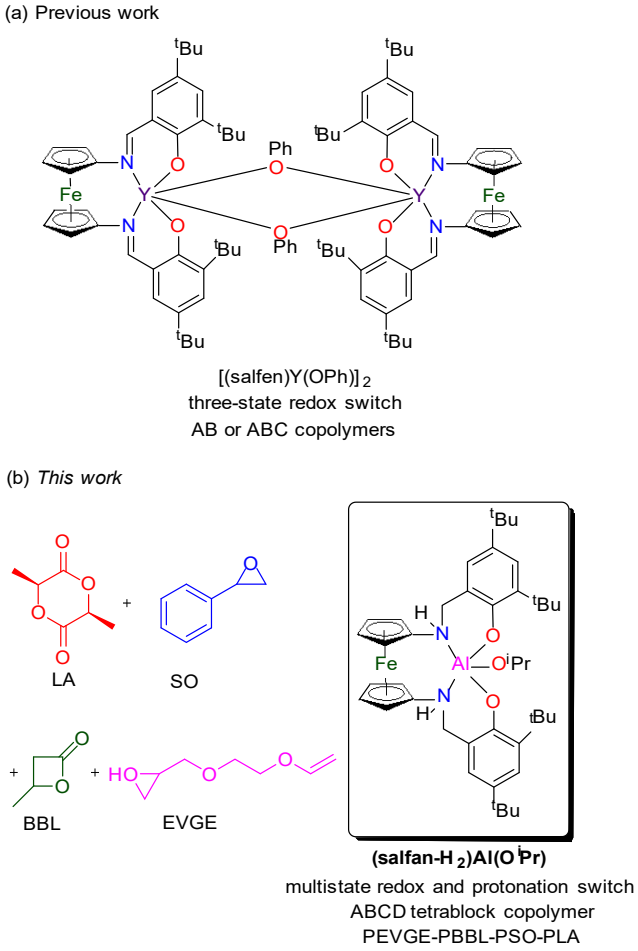


Figure 1. (a) Previously reported yttrium three state redox switch; (b) Novel ferrocene aluminum complex, a four state redox and protonation switch, capably of forming ABCD tetrablock copolymers.

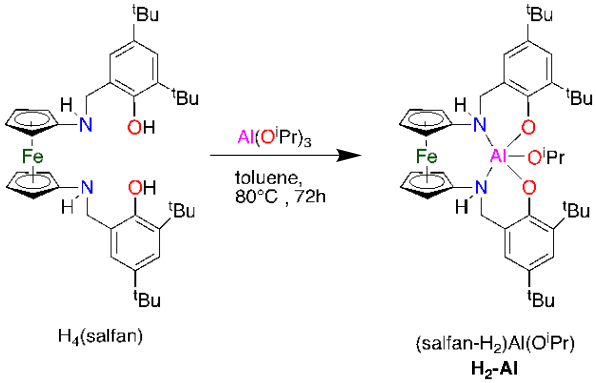
Results and discussion

Synthesis and characterization of (salfan-H$_2$)Al(O^{i}Pr) (H$_2$-Al). Compound **H$_2$-Al** was synthesized by the reaction of H$_4$(salfan) with Al(O^{i}Pr)$_3$ (Figure 2), and characterized by ^{1}H, ^{13}C, and heteronuclear single quantum coherence (HSQC) NMR spectroscopy at -38 °C, 25 °C, and 100 °C (Figures S1–S3). At 25 °C (Figure S2), the ferrocene and amine peaks were obscured, with only one peak observed for the phenyl oxide, ortho and para *tert*-butyl, and *iso*-propoxide protons. To obtain a clear resolution of the ferrocene and amine peaks, low temperature (-38 °C) and high temperature (100 °C) measurements were performed. At -38 °C, 10 peaks were identified, including 2 corresponding to ferrocene and amine that were further confirmed and analyzed using ^{13}C and HSQC NMR spectroscopy (Figure S1). Furhtermore, the solid-state molecular structure revealed a tetrahedral coordination at the aluminum center, with one metal-N distance notably shorter than the other (Figure 2). Notably, this differs from the structure of the previously reported ferrocene-aluminum (salfen)Al(OiPr),[62] which features a pentacoordinate aluminum center.

We examined the redox behavior of compound **H$_2$-Al** through in situ redox reactions employing ^{Ac}FcBAr^F (^{Ac}Fc = acetylferrocene, BAr^F = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) as an oxidant and CoCp$_2$ as a reductant in C$_6$D$_6$ (Scheme 2 left). These reactions were monitored using ^{1}H NMR spectroscopy with an internal standard (Figure S4). Upon adding an equivalent of oxidant, a rapid color change occurred, shifting from yellow-orange to dark purple, accompanied by the disappearance or shift of most ^{1}H NMR peaks, consistent with the formation of [(salfan-H$_2$)Al(O^{i}Pr)][BAr^F]. Subsequently, CoCp$_2$ was introduced, leading to the recovery of approximately 72% of the reduced compound.

In situ synthesis and characterization of [(DBU)$_2$][(salfan)Al(O^{i}Pr)]. With two protons present on the amine groups, we hypothesized that a deprotonated structure could yield unique reactivity. Our methodology involved titrating a 0.1 M stock solution of (salfan-H$_2$)Al(OiPr) in C$_6$D$_6$ with a base, specifically 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as depicted in Scheme 2 (Figure S5). Significantly, as we incrementally introduced more base into the system, the peaks corresponding to ferrocene and the amine shifted. After adding 2 equivalents of DBU, these shifts became negligible.

Further examination of this process was carried out using UV-Vis spectroscopy (Figure 3a). The introduction of additional base resulted in a rightward shift in the wavelength λ_{max}, accompanied by an increase in absorbance. After approximately 2 equivalents of base were added, the change in λ_{max} became less pronounced (Figure 3b), similar to the ^{1}H NMR results.



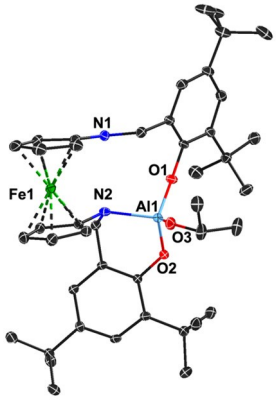
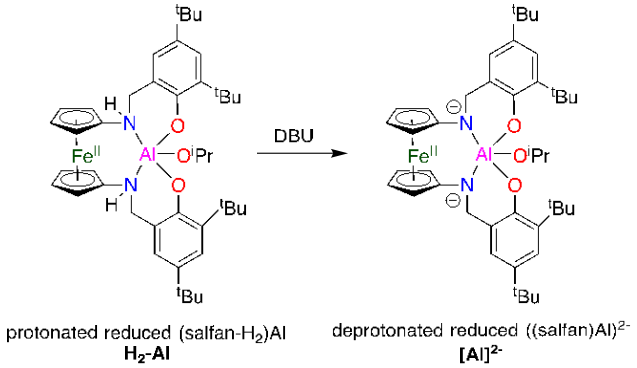


Figure 2. Synthetic route to (salfan-H$_2$)Al(O^{i}Pr) (top) and its molecular structure (bottom), hydrogen atoms were omitted for clarity.



Scheme 1. Protonated state switch of (salfan-H2)Al(OiPr) to (salfan)Al(OiPr) by adding DBU.

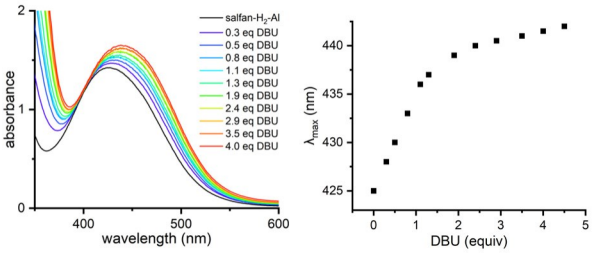
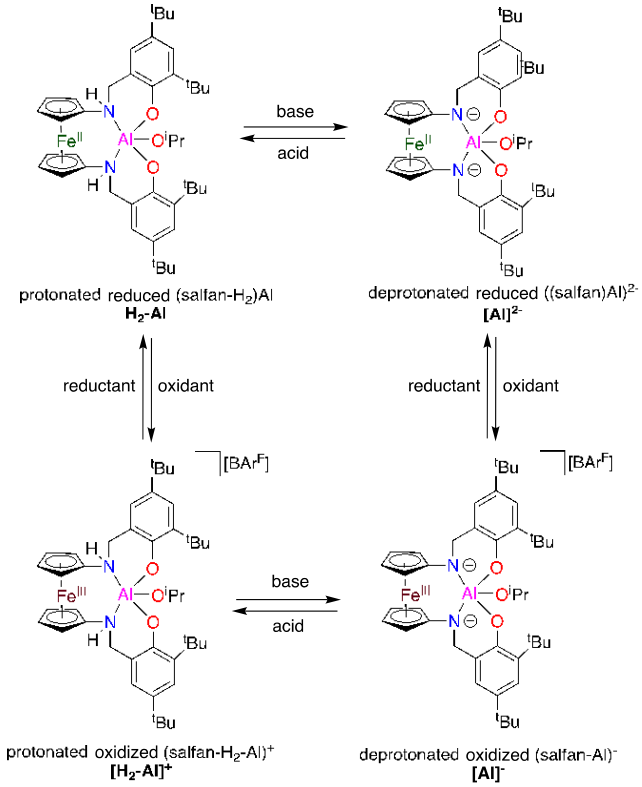


Figure 3. (a) UV-Vis spectra of (salfan-H2)Al(OiPr) titrated with DBU. (b) λ_{max} of the system versus the equivalent of base added.



Scheme 2. Redox and protonated state switch between the four states of (salfan-H2)Al(OiPr).

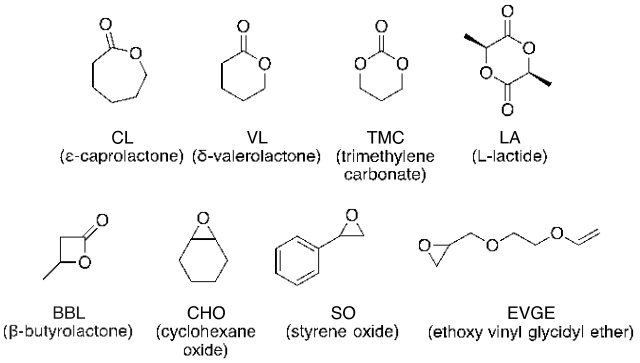


Figure 4. Monomers studied for investigating homopolymerization reactivity.

In subsequent reactions employing the fully deprotonated state, we introduced two equivalents of DBU to ensure the complete deprotonation of the compound. Following full deprotonation, we added 2-chloropyridinium triflate (OTf) and studied the system using ^{1}H NMR (Figure S6) and UV-Vis spectroscopy (Figure S7) to investigate the amount of acid required to protonate [(DBU)2][(salfan)Al(OiPr)] back to its original state, (salfan-H2)Al(OiPr). The addition of acid resulted in a shift in λ_{max} and an increase in absorbance until 24.7 equivalents of acid was added. Based on the λ_{max} of (salfan-H2)Al(OiPr), approximately 20 equivalents of 2-chloropyridinium triflate was required to protonate [(DBU)2][(salfan)Al(OiPr)] back to (salfan-H2)Al(OiPr). This confirmation established the system's ability to switch between four states (as shown in Scheme 1), making it suitable for further applications in copolymerization.

Homopolymerization reactions. Our investigation focused on the reactivity of the new system toward cyclic esters, including L-lactide (LA), ϵ-caprolactone (CL), δ-valerolactone (VL), β-butyrolactone (BBL), and trimethylene carbonate (TMC), as well as epoxides, including cyclohexene oxide (CHO), styrene oxide (SO), and ethoxy vinyl glycidyl ether (EVGE), listed in Figure 4. The resulting homopolymers were characterized by size exclusion chromatography (SEC, Figure S29-45) and NMR spectroscopy (Figure S46-62).

TMC, VL, and CL demonstrated activity across all four states (Table 1, entries 1a-1d, 2a-2d, 3a-3d), while LA displayed selectivity toward the catalyst's protonated reduced state (Table 1, entry 4a). In contrast, BBL exhibited selectivity in the deprotonated reduced state (Table 1, entry 5c), while EVGE displayed selectivity in the deprotonated oxidized state (Table 1, entry 8d). Both SO (Table 1, entry 7b) and CHO (Table 1, entry 6b) exhibited selectivity with the protonated state at 25°C, both achieving a maximum monomer conversion of 100% within 2 hours. However, CHO exhibited a broad SEC peak and high dispersity (Figure S11-27), and consequently, is not a favorable choice for subsequent copolymerizations.

Given the selectivity of (salfan-H2)Al(OiPr) for L-lactide (LA) in its protonated reduced state (Table 1, entry 4a-4d), we conducted an in situ selectivity study focusing on this monomer (Figure S8). Starting from the protonated reduced state, the polymerization of LA by (salfan-H2)Al(OiPr) reached a 18.7% conversion after 5 hours at 100 °C. Upon oxidation with ^{Ac}FcBAr^F, the polymerization was temporarily halted. However, upon introducing CoCp2 into the reaction mixture, the polymerization resumed at a rate similar to before the switch and reached 35% conversion in 14.4 hours. Interestingly, when

DBU was added to transform it into the deprotonated reduced state, DBU rapidly converted LA into an oligomer, achieving 100% conversion in just 5 minutes.

Therefore, we decided to shift our focus to selectivity studies with VL, as it exhibited a good activity in both the protonated reduced state and deprotonated oxidized state (Table 1, entry 2a-2d). Starting with (salfan-H_2)Al(OiPr), the polymerization reached 28.4% conversion after 41 minutes at 25°C (Figure 5). Upon the addition of ^{Ac}FcBAr^{F}, the polymerization activity slowed considerably, reaching a 43.2% conversion in 118 minutes. The activity was reestablished by adding DBU, which transformed the catalyst into the deprotonated oxidized state, ultimately reaching 56.4% conversion in 150 minutes. The polymerization was then halted by introducing $CoCp_2$ to revert it to the deprotonated state. Subsequently, the polymerization resumed upon adding acid to switch it back to the protonated reduced state, reaching a maximum conversion at 73% in 258 minutes. This study further confirms the compound's four-state in situ orthogonality, effectively established during the polymerization process.

Copolymerization reactions. Given the specific monomer selectivity observed for LA, SO, BBL, and EVGE and the low dispersity (<1.3) of the corresponding polymers, we decided to synthesize copolymers by strategically switching between different states of the compound. Employing a sequential addition method (Scheme 5), we initiated the process with the protonated reduced state of (salfan-H_2)Al(OiPr), **H_2-Al**. After reaching maximum conversion for the first monomer, LA, we introduced ^{Ac}FcBAr^{F} to transition the catalyst to the protonated oxidized compound state, **[H_2-Al]$^+$**.

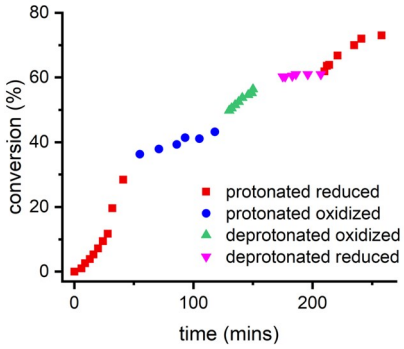


Figure 5. Plot of polymerization conversion vs time of 100 equivalent VL in C_6D_6 using in situ redox and protonation reactions with ^{Ac}FcBAr^{F}, $CoCp_2$, DBU, and [2-chloropyridinium][OTf].

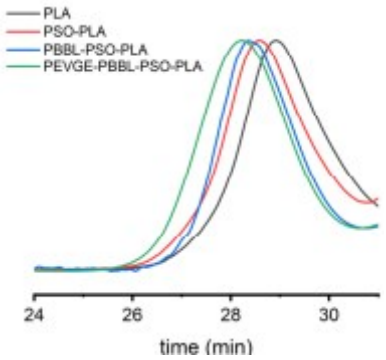


Figure 6. Normalized SEC traces of each stage of PEVGE-PBBL-PSO-PLA sequential formation.

Subsequently, the second monomer, SO, was added, and after 16 hours, an AB diblock copolymer, PSO-PLA, was formed. $CoCp_2$ and DBU were then introduced to convert the catalyst to the deprotonated reduced state, **[Al]$^{2-}$**, followed by the addition of BBL. After 24 hours, the ABC triblock copolymer PBBL-PSO-PLA was successfully synthesized. ^{Ac}FcBAr^{F} was once again added to the system to transition the catalyst to the deprotonated oxidized state, **[Al]$^-$**, and EVGE was introduced. Within 24 hours, the ABCD tetrablock copolymer PEVGE-PBBL-PSO-PLA was formed (Figure S9).

Following the isolation of the copolymers, their characterization was carried out using diffusion ordered spectroscopy (DOSY, Figure S27) and SEC (Figure 6). DOSY confirmed the successful synthesis of all block copolymers. To circumvent the formation of random block copolymers, we prioritized the use of monomers with single selectivity, with EVGE emerging as the most suitable candidate among those tested. Notably, this represents the first instance of an ABCD tetrablock copolymer produced through the utilization of a multistate switchable catalyst system.

Given the distinct selectivity of the monomers, the feasibility of a one-pot reaction was also explored. By easily altering the catalyst's state, we successfully synthesized PEVGE-PBBL-PSO-PLA in a single reaction vessel. This achievement was validated through through characterization using ^{1}H NMR, DOSY, and SEC (Figure S63-65).

Conclusion

We introduced a ferrocene-aluminum compound with tunable redox and protonation properties, serving as a catalyst for ring-opening polymerization. Through the utilization of this versatile, multistate system, we successfully synthesized a variety of innovative copolymers, including AB diblock (PSO-PLA), ABC triblock (PBBL-PSO-PLA), and ABCD tetrablock copolymers (PEVGE-PBBL-PSO-PLA). These copolymers were obtained through both sequential addition and a one-pot reaction. This adaptable system not only expands the range of available monomers but also facilitates the incorporation of diverse monomer units, resulting in unique microstructure copolymers. Our ongoing research aims to explore further applications and develop even more versatile copolymers.

Supporting Information

Experimental and characterization data, NMR spectra, and SEC data (PDF)

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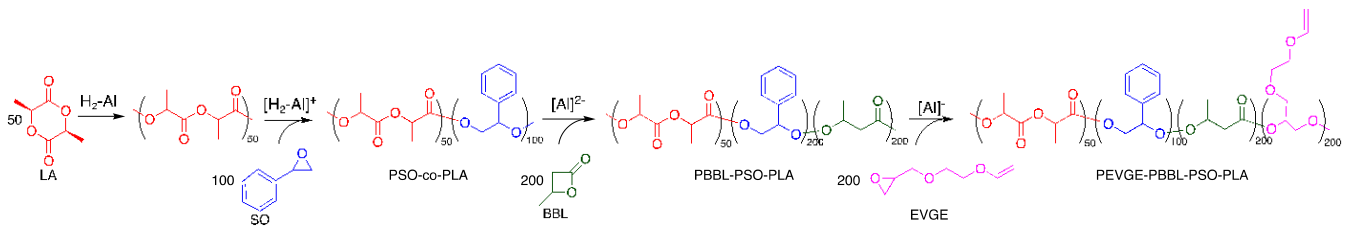
Table 1. Homopolymerization of various cyclic esters and epoxides by the four states of (salfen)Al(OiPr).

	monomer	cat. state	temp (°C)	equiv	time (h)	conv. (%)	$Đ$	$M_{n,calc}$ (kDa)	$M_{n,exp}$ (kDa)	$M_{w,exp}$ (kDa)
1a	CL	H_2-Al	25	110	5	85	1.3	10.7	12.1	14.2
1b		$[H_2\text{-Al}]^+$	25	80	22	90	1.1	8.2	11.1	12.3
1c		$[Al]^{2-}$	25	80	24	52	1.0	4.8	8.3	8.6
1d		$[Al]^-$	25	73	5	93	1.1	7.8	14.0	15.9
2a	VL	H_2-Al	25	100	5	84	1.1	8.4	6.4	6.8
2b		$[H_2\text{-Al}]^+$	25	92	48	22	-	-	-	-
2c		$[Al]^{2-}$	25	75	48	40	1.0	3.0	3.9	3.8
2d		$[Al]^-$	25	100	5	85	1.1	8.5	12.8	13.9
3a	TMC	H_2-Al	25	100	1.5	100	1.3	10.2	11.6	14.8
3b		$[H_2\text{-Al}]^+$	25	85	4	100	1.1	8.4	7.9	8.6
3c		$[Al]^{2-}$	25	70	20	100	1.1	7.2	6.4	6.9
3d		$[Al]^-$	25	70	5	97	1.1	6.9	7.8	8.6
4a	LA	H_2-Al	100	92.5	52	87	1.1	11.6	14.2	15.0
4b		$[H_2\text{-Al}]^+$	100	100	NR	-	-	-	-	-
4c		$[Al]^{2-}$	100	50	NR	-	-	-	-	-
4d		$[Al]^-$	100	80	NR	-	-	-	-	-
5a	BBL	H_2-Al	100	70	NR	-	-	-	-	-
5b		$[H_2\text{-Al}]^+$	100	100	NR	-	-	-	-	-
5c		$[Al]^{2-}$	100	160	19	63	1.2	8.68	7.42	9.16
5d		$[Al]^-$	100	100	NR	-	-	-	-	-
6a	CHO	H_2-Al	100	80	NR	-	-	-	-	-
6b		$[H_2\text{-Al}]^+$	25	100	0.5	100	1.8	9.0	36.3	66.0
6c		$[Al]^2$	100	80	NR	-	-	-	-	-
6d		[Al]	25	100	NR	-	-	-	-	-
7a	SO	H_2-Al	100	72	NR	-	-	-	-	-
7b		$[H_2\text{-Al}]^+$	25	110	2hr	100	1.1	13.2	13.6	15.0
7c		$[Al]^{2-}$	100	93	NR	-	-	-	-	-
7d		$[Al]^-$	100	72	NR	-	-	-	-	-
8a	EVGE	H_2-Al	100	75	NR	-	-	-	-	-
8b		$[H_2\text{-Al}]^+$	100	75	NR	-	-	-	-	-
8c		$[Al]^{2-}$	100	100	NR	-	-	-	-	-
8d		$[Al]^-$	100	100	48	100	1.3	14.1	28.3	35.7

LA = L-lactide, CL = ϵ-caprolactone, VL = δ-valerolactone, BBL = β-butyrolactone, TMC = trimethylene carbonate, CHO = cyclo-hexene oxide, SO = styrene oxide, EVGE = ethoxy vinyl glycidyl ether, NR = no reaction.



Scheme 5. Synthesis of ABCD block copolymers by sequential addition.

Table 2. Redox and protonation state controlled copolymerization by (salfan-H_2)Al(O^iPr) via sequential addition.

	Monomers	Cat. State	Temp (°C)	Equiv	Time (h)	Conv. (%)	Đ	$M_{n,calc}$ (kDa)	$M_{n,exp}$ (kDa)	M_{wexp} (kDa)
1	LA	H_2-Al	100	56	48	92	1.1	7.43	6.48	7.13
2	LA-SO	H_2-Al - $[H_2\text{-Al}]^+$	25	100	16	100	1.1	19.5	14.0	15.0
3	LA-SO-BBL	H_2-Al - $[H_2\text{-Al}]^+$ - $[Al]^{2-}$	100	201	24	100	1.1	36.7	18.9	19.7
4	LA-SO-BBL-EVGE	H_2-Al - $[H_2\text{-Al}]^+$ - $[Al]^{2-}$ - $[Al]^-$	100	200	24	100	1.6	65.5	28.9	45.0

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Notes

The authors declare no competing financial interest.

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