

Cite this paper: *Chin. J. Chem.* **2022**, *40*, 21–27. DOI: 10.1002/cjoc.202100569

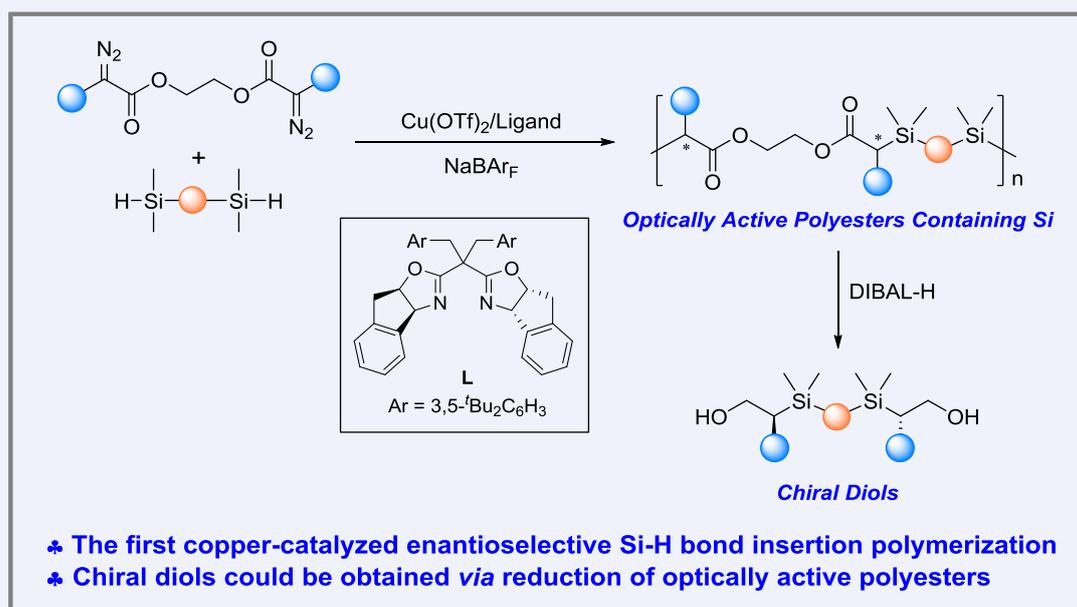
Copper-Catalyzed Si—H Bond Insertion Polymerization for Synthesis of Optically Active Polyesters Containing Silicon

 Xiao-Yong Zhai,^{†,a} Xiao-Qing Wang,^{†,a} Bo Wu,^{*,a} and Yong-Gui Zhou^{*,a,b}
^aState Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, Liaoning 116023, China

^bState Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

Comprehensive Summary

The synthesis and characterization of chiral polymers with diverse structure remain a long-term challenging research topic. Herein, a copper-catalyzed enantioselective insertion of carbene into Si—H bond was applied to polycondensation, giving a new type of optically active degradable polyesters containing Si—C bond in the main chain. The polymerization features mild condition, broad substrate scope, excellent yields and enantioselectivities. Chiral diols could be obtained via reduction of optically active polyesters. Thermogravimetric analysis indicated these chiral polyesters exhibit good thermal stability.



Keywords

Polymerization | Insertion | Asymmetric catalysis | Optically active polyesters | Copper

 *E-mail: bowu@dicp.ac.cn; ygzhou@dicp.ac.cn

†These authors contributed equally to this work.

[View HTML Article](#)
[Supporting Information](#)

Background and Originality Content

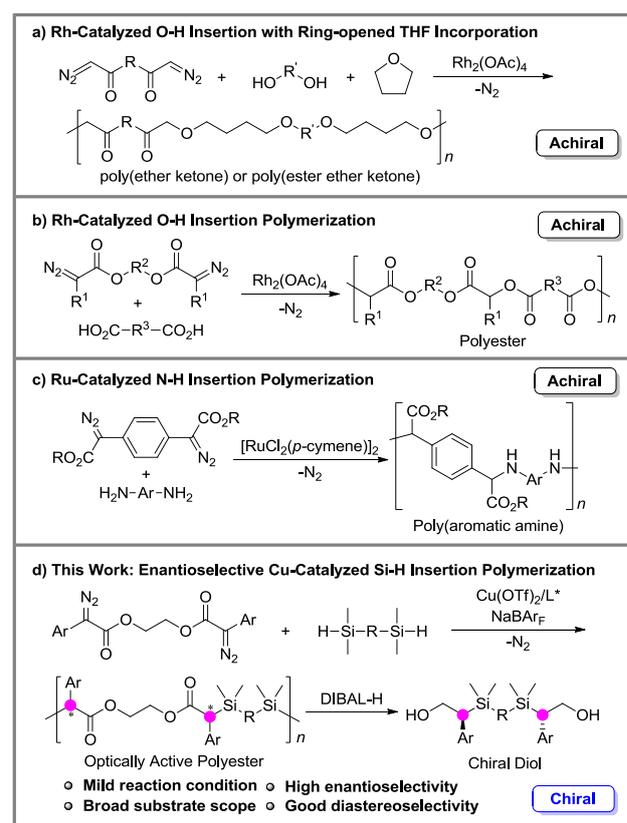
Naturally occurring optically active macromolecules, such as polypeptides, polynucleotides and polysaccharides, exist widely in every aspect of life.^[1] Optically active polymers have been widely utilized in chiral recognition and resolution, liquid crystallization, asymmetric reaction, and lately in circularly polarized light (CPL) generation and play vital roles in realizing highly sophisticated functions in a living system, which inspire the interest in studying chiral synthetic polymers. In contrast to natural optically active polymers, the absolute configuration of chiral synthetic polymers can be adjusted by changing chiral catalyst. Gradually, dense interest in chiral synthetic polymers has been focused on the polymerization mechanism, conformational properties and modeling natural polymers.^[2-4] In the past few decades, great efforts have been spent on the developing new kind of chiral polymers, which gradually show potential in the fields of chiral catalysis, separation media, biomaterials, and materials for nonlinear optics.^[5-7]

Even though considerable success has been made for the synthesis of chiral polymers from enantioenriched monomers,^[8] this method suffers from high cost and commercial unavailability of enantioenriched monomers. By comparison, the synthesis of optically active polymers via asymmetric polymerization of achiral monomers is more promising, economical and acceptable.^[2,9] Up to now, different types of optically active polymers have been synthesized via asymmetric polymerization, including poly(maleimide)s, poly(quinoxaline)s, polyesters, polyketones, etc.^[10-31] However, the characterization of the chirality of optically active polymers is often achieved by the results of optical rotations and circular dichroism, which is not beneficial to the precise characterization of the optical purity of chiral polymers. Thus, determination of the optical purity of the chiral polymers is still a challenging research topic.^[32-34]

As an efficient method to construct C—C and C—X bond, carbene insertion reactions have been widely applied in organic synthesis.^[35-39] Due to the highly synthetic potential of the generated building blocks, transition metal-catalyzed carbene insertion reactions have attracted much attention.^[40] In consideration of the highly reactivity of diazocarbonyl compounds and the efficiency of insertion reaction, this efficient approach has been gradually utilized in the synthesis of polymer with unprecedented main-chain structure. The first example of insertion polymerization of diazocarbonyl compounds was developed by Ihara group.^[41] In this work, a three-component polycondensation of bisphenols, bis(diazocarbonyl) compounds and THF was realized by employing $\text{Rh}_2(\text{OAc})_4$ as a catalyst, affording a new type of poly(ether ketone)s. The polycondensation consists of ring-opening reaction of THF and O—H bond insertion reaction of carbene (Scheme 1a). Moreover, dicarboxylic acids were also proved to be suitable for this three-component polycondensation, realizing the synthesis of poly(ester ether ketone)s (Scheme 1a).^[42] Polyesters are an important class of polymers possessing excellent mechanical properties, degradability and easy processability.^[43-44] To enrich methodologies for polyester synthesis, the group of Yan developed Rh-catalyzed O—H bond insertion polymerization of diazocarbonyl compounds and dicarboxylic acids, providing a variety of polyesters (Scheme 1b).^[45] Recently, Ru-catalyzed N—H bond insertion polymerization of bis(diazoacetate) with dianiline was also reported, delivering a series of well-defined polyamines containing NH in the polymer main chain (Scheme 1c).^[46]

Transition-metal-catalyzed enantioselective Si—H bond insertion reactions of carbenes have served as a straightforward and efficient method for the preparation of chiral silane-containing compounds.^[47-51] In 2008, Zhou and coworkers disclosed elegant copper-catalyzed Si—H bond insertion reactions, providing a wide range of α -silylestere with excellent enantioselectivities and

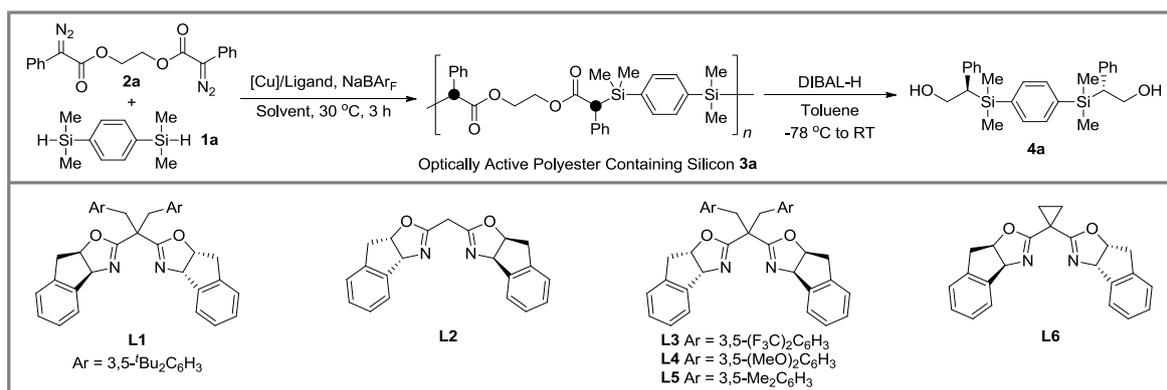
Scheme 1 Metal-catalyzed X—H insertion polymerization



high yields.^[51] Owing to the importance of chiral polymers containing silicon and our interests in the synthesis of optically active polymers,^[52-55] we envisioned that the asymmetric Si—H insertion reaction can be applied to polycondensation, giving optically active polymers containing Si—C bond in the main chain. In order to precisely characterize the optical purity of optically active polymers, the structure of monomer was designed by introducing ester group into the linker of diazo compounds. Therefore, the resulting polymers could be reduced to chiral diols, which is convenient for the precise characterization of the chirality of optically active polymer. Herein, we report the first enantioselective copper-catalyzed Si—H bond insertion polymerization, providing highly optically active polyesters (Scheme 1d). Chiral diols could be obtained *via* the selective reduction of optically active polyesters.

Results and Discussion

In the initial study, the insertion reaction of silane (**1a**) with diazocarbonyl compound (**2a**) was performed in dichloromethane at 30 °C with 2 mol% copper catalyst prepared *in situ* from $\text{Cu}(\text{OTf})_2$, bisoxazoline ligand **L1** and NaBAR_f (Table 1). A preliminary investigation revealed that optically active polymer **3a** was obtained with good M_n and moderate yield (Table 1, entry 1). In order to precisely characterize the optical purity of polymer **3a**, the diisobutylaluminum hydride was applied to selective cleavage of polymer. To our delight, chiral diol **4a** was obtained with high stereoselectivity (99.0% *ee*, 94 : 6 *dr*). According to literature report,^[56] increasing the amount of NaBAR_f may improve both the yield and the enantioselectivity. Encouraged by this, when the amount of NaBAR_f was increased to 2 equivalent relative to $\text{Cu}(\text{OTf})_2$, the yield and M_n were markedly improved, and the enantioselectivity was maintained (entry 2). Then the effect of solvents was conducted (entries 4–6). It was found that solvents

Table 1 Optimization of reaction parameters^a

entry	NaBAR _F (2x mol%)	solvent	[Cu]	L	M _n ^b /(kg·mol ⁻¹)	PDI ^b	yield of 3a ^c /%	ee of 4a ^d /%	dl/meso of 4a ^d
1	1.2	DCM	Cu(OTf) ₂	L1	9.3	1.90	73	99	94 : 6
2	2	DCM	Cu(OTf) ₂	L1	11.6	2.07	91	99	94 : 6
3	3	DCM	Cu(OTf) ₂	L1	10.9	1.96	82	99	94 : 6
4	2	CHCl ₃	Cu(OTf) ₂	L1	5.5	1.51	63	99	95 : 5
5	2	PhCl	Cu(OTf) ₂	L1	—	—	—	—	—
6	2	THF	Cu(OTf) ₂	L1	—	—	gel	—	—
7	2	DCM	CuOTf·1/2PhH	L1	4.7	1.45	60	99	96 : 4
8	2	DCM	Cu(CH ₃ CN) ₄ BF ₄	L1	2.6	1.52	79	99	96 : 4
9	2	DCM	Cu(CH ₃ CN) ₄ PF ₆	L1	3.9	1.55	7	99	92 : 8
10	2	DCM	Cu(OTf) ₂	L2	9.8	1.84	90	-99	88 : 12
11	2	DCM	Cu(OTf) ₂	L3	—	—	—	—	—
12	2	DCM	Cu(OTf) ₂	L4	12.7	2.11	92	-99	91 : 9
13	2	DCM	Cu(OTf) ₂	L5	11.5	1.95	90	-99	95 : 5
14	2	DCM	Cu(OTf) ₂	L6	—	—	—	—	—

^a Reaction conditions: monomer (0.3 mmol), [Cu] (2 mol%), L (2.4 mol%), NaBAR_F (2x mol%), 30 °C, 3 h, solvent (1.5 mL). ^b Determined by GPC with RI.

^c Isolated yield. ^d Measured by chiral HPLC.

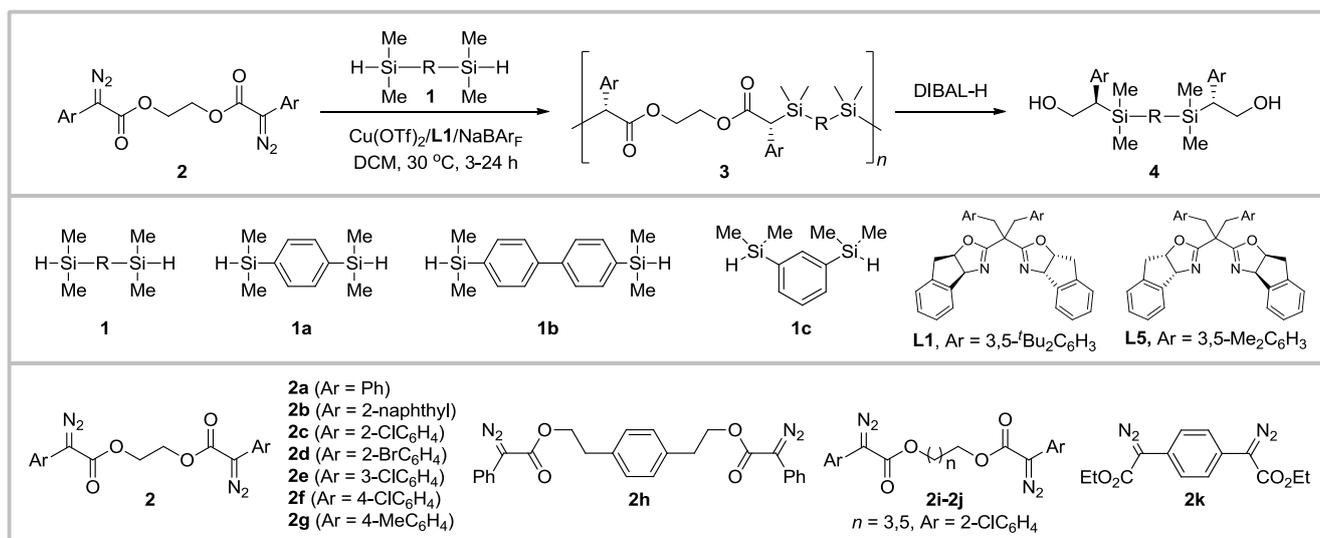
play a crucial role in polymerization. Good stereoselectivity and better PDI could be obtained in CHCl₃ albeit with lower reactivity and molecular weight (entry 4). The polymerization was failed to deliver **3a** in PhCl and THF. Next, the effect of metal precursor was investigated (entries 7–9). Although better stereoselectivity could be obtained by using CuOTf·1/2PhH or Cu(CH₃CN)₄BF₄, the polymerization employing these metal precursors suffered from low M_n and yields (entries 7–8). Finally, a systematic chiral ligand screening was carried out (entries 10–14). To our delight, bisoxazoline ligands containing different electron-donating group all resulted in high molecular weight, excellent stereoselectivity and good reactivity. By contrast, the use of bisoxazoline ligand containing electron-withdrawing group would inhibit polymerization (entry 11). When **L2** was used as ligand, **3a** exhibited narrow PDI while low molecular weight, probably due to the less steric hindrance of bisoxazoline skeleton (entry 10). Unfortunately, **3a** was not detected when using ligand containing cyclopropane linker (entry 14). Considering the molecular weight and stereoselectivity, the optimal reaction conditions were established as: Cu(OTf)₂ (2 mol%), chiral bisoxazoline ligand **L1** (2.4 mol%), NaBAR_F (4 mol%), DCM (1.5 mL), 30 °C.

Next, the substrate scope of copper-catalyzed Si—H insertion polymerization was investigated under the optimized conditions (Table 2). Firstly, silanes containing different aromatic backbones were investigated by the reaction with diazocarbonyl compound **2a** (entries 1–3). Nevertheless, the results indicated that backbones of these silanes had marginal influence on the stereoselectivity of the polymerization, albeit with lower molecular weight. For example, the asymmetric polymerization produced the enantiopure product **3b** in 96% yield, 99% ee with molecular weight of 9100 (entry 2). Then, silane **1a** was chosen to react with various

diazocarbonyl compounds. The replacement of phenyl group with steric hindrance naphthyl group resulted in polymer with M_n of 11.2 kg/mol and good stereoselectivity (99% ee and 93.5 : 6.5 dl/meso) (entry 4). Moreover, the polymerization could tolerate both electron-donating and electron-withdrawing substituents (**2c**–**2g**). By introducing electron-withdrawing group such as –Cl, –Br onto *ortho*-position of aromatic ring, polyesters were provided with high M_n, yield and excellent stereoselectivity (entries 5–6). It was found that the enantioselectivity was slightly affected when the –Cl was introduced onto the *para*-position (**2f**) or the *meta*-position (**2e**) (entries 7–8). Additionally, diazocarbonyl compound **2g** containing electron-donating methyl group on the aromatic ring gave the best stereoselectivity (99% ee and 99 : 1 dl/meso), good reactivity and high molecular weight (entry 9). In a similar fashion, a diverse array of **2** with different chain length links could react smoothly, giving the corresponding optically active polyesters **3k**–**3l** with high enantioselectivity and molecular weight (entries 11–12). It's worth to mention that **2h** was also well compatible to deliver the corresponding product with 92% yield and M_n of 12 000 (entry 10). Finally, a diazocarbonyl compound **2k** containing aromatic linker was applied to the polymerization, giving chiral polymer **3m** with moderate M_n and yield (entry 13). Due to the fact that no ester group exists in the main chain of polymer **3m**, the precise characterization of the optical purity of chiral polymer **3m** could not be realized through selective cleavage.

The well-defined structure of optically active polyesters containing silicon in the main chain was confirmed by ¹H, ¹³C and ²⁹Si NMR spectra (Figures S36–S74 in the Supporting Information). For polymer **3b** (Scheme 2), the aromatic protons appeared at δ 7.61–7.48, 7.47–7.35 and 7.30–7.16. The proton of CH of chiral

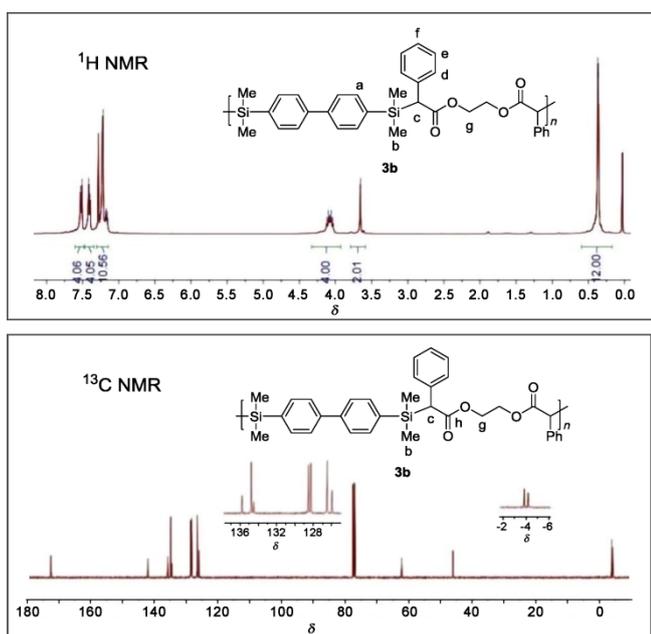
Table 2 Substrate scope^a



entry	1	2	Yield of 3 ^f /%	M_n^b /(kg·mol ⁻¹)	PDI ^b	ee of 4 ^d /%	dl/meso of 4 ^d	T _g ^e /°C
1	1a	2a	91 (3a)	11.6	2.07	99	94 : 6	21.7
2 ^f	1b	2a	96 (3b)	9.1	2.43	99	94 : 6	38.9
3 ^f	1c	2a	78 (3c)	6.1	1.73	98	94 : 6	16.6
4	1a	2b	94 (3d)	11.2	1.90	99	93.5 : 6.5	42.6
5	1a	2c	89 (3e)	14.6	1.82	99	97 : 3	14.3
6	1a	2d	99 (3f)	10.9	1.87	99	97 : 3	19.1
7 ^g	1a	2e	67 (3g)	8.5	1.80	99	94.5 : 5.5	14.8
8	1a	2f	83 (3h)	9.6	1.78	99	95 : 5	41.5
9	1a	2g	92 (3i)	11.3	1.99	99	99 : 1	25.8
10 ^h	1a	2h	92 (3j)	12.0	2.10	94	96 : 4	13.2
11	1a	2i	79 (3k)	11.6	1.96	99	98 : 2	12.7
12	1a	2j	91 (3l)	13.5	1.98	99	98 : 2	4.6
13 ⁱ	1a	2k	64 (3m)	11.3	1.76	—	—	3.3

^a Reaction conditions: monomer (0.3 mmol), Cu(OTf)₂ (2 mol%), L1 (2.4 mol%), NaBAR_f (4 mol%), 30 °C, 3 h, DCM (1.5 mL). ^b Determined by GPC with RI. ^c Isolated yield. ^d Measured by chiral HPLC. ^e Determined by DSC. ^f Reaction conditions: L5 (2.4 mol%), 24 h. ^g Reaction conditions: 24 h. ^h Reaction conditions: L5 (2.4 mol%), 24 h. ⁱ Reaction conditions: 12 h.

Scheme 2 NMR spectra analysis of chiral polyester 3b



carbon in main-chain was located at δ 3.66. And CH₂ protons (H_g) splitting into a multiple were situated at δ 4.33–3.93. The ¹³C NMR spectrum further supported the formation of desired 3b, because characteristic resonances from the backbone were clearly discerned. The singlet at δ 172.5 was assigned to C_h, and the singlet at 62.2 was assigned to C_g. Furthermore, the chiral carbon C_c in main-chain was located at δ 46.1.

After purification, thermal properties of the polyesters containing silicon in the main chain were investigated under nitrogen atmosphere using TGA (Table 3) and DSC (Table 2). All of the tested polyesters exhibited good thermal stability, T₅ values ranged from 276 °C to 331 °C, and T₅₀ values varied from 379 °C to 410 °C. Owing to the aromatic link in polymer (–)3j, it had a relatively higher T₅₀ value (Table 3, entry 2). Additionally, a diverse array of 3 with different chain length link showed similar T₅ and T₅₀ values. All of enantiopure polyesters exhibited glass transition temperatures via DSC. However, the T_g values of these polymers were quite different, which might depend on the substituents on the polyesters. And (+)-3d had the highest glass transition temperature by applying monomer 2b containing rigid backbone (Table 2, entry 4). Introducing –Cl onto *para*-position of aromatic ring ensured (+)-3h with more regular structure comparing to (+)-3e or (+)-3g, thus (+)-3h exhibited higher glass transition temperature (Table 2, entries 5, 7, 8). In contrast to (+)-3e

and (+)-**3k**, the T_g of (+)-**3l** could be decreased to 4.6 °C by applying monomer **2j** with long chain length link (Table 3, entries 3–5). And we hope these enantiomerically enriched polymers with good thermal stability would expand the application in chiral catalysis, separation media, biomaterials or materials for nonlinear optics in the future.

Table 3 Thermal analysis of polyesters^a

Entry	Polyester 3	$T_5^a/^\circ\text{C}$	$T_{50}^a/^\circ\text{C}$	$T_g^b/^\circ\text{C}$
1	(+)- 3a	276	399	21.7
2	(-)- 3j	289	410	13.2
3	(+)- 3e	312	382	14.3
4	(+)- 3k	324	386	12.7
5	(+)- 3l	331	379	4.6

^aTemperature at which 5% or 50% mass loss is observed under N₂ by TGA.

^bDetermined by DSC.

Conclusions

In summary, we have demonstrated that Cu-catalyzed asymmetric Si—H insertion of diazocarbonyl compounds with silanes could be successfully applied to polycondensation, providing a series of optically active polyesters containing silicon in the main chain (up to 99% yield, 14.6 kg/mol). In order to realize the purpose of precise characterization of the resulting chiral polymers, ester group was introduced into the linker of diazocarbonyl compounds. Chiral diols with high yields and stereoselectivities (up to 92% yield, 99% *ee* and 99 : 1 *dr*) were obtained by the reduction of chiral polymers **3** employing DIBAL-H as a reductant. Further study will focus on the transition-metal-catalyzed asymmetric heteroatom-hydrogen bond insertion polymerization.

Experimental

General procedure for the asymmetric polymerization. To an oven-dried 25 mL resealable Schlenk flask equipped with a magnetic stir bar was charged with Cu(OTf)₂ (2.1 mg, 0.0060 mmol), chiral ligand **L1** (5.3 mg, 0.0072 mmol), NaBAR_F (10.6 mg, 0.0120 mmol) and DCM (1.0 mL) under nitrogen. The solution was stirred at room temperature for 2 h. Then, monomer silanes **1** (0.3 mmol), diazocarbonyl compounds **2** (0.3 mmol) and DCM (0.5 mL) were added into the flask under nitrogen. The flask was stirred at 30 °C for 3 h under nitrogen. After polymerization, the reaction mixture was purified by the precipitation method.

General procedure for cleavage of polyesters. To a nitrogen-filled flask were added polymers **3** (60 mg) and toluene (3 mL). Then, DIBAL-H (0.5 mL, 1.5 mol/L in toluene) was added dropwise to the flask at -78 °C. The reaction mixture was stirred at -78 °C for 0.5 h. Then, the mixture was allowed to warm to room temperature and stirred for 3 h. After the reaction, the reaction mixture was quenched by slow addition of methanol (2 mL). To the mixture were added an aqueous solution of Rochelle salt (2 g in 15 mL water) and ethyl acetate (15 mL). The mixture was stirred vigorously. Then the aqueous layer was extracted with ethyl acetate (20 mL × 3). The combined organic layer was dried over sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (50 : 1–20 : 1 hexanes : ethyl acetate) to give the chiral diols **4**.

Supporting Information

The supporting information for this article is available on the WWW under <https://doi.org/10.1002/cjoc.202100569>.

Acknowledgement

Financial support from the National Natural Science Foundation of China (21690074), Dalian Institute of Chemical Physics (UN201701) and the Chinese Academy of Sciences (XDB17020300) is acknowledged.

References

- [1] Itsuno, S. *Polymeric Chiral Catalyst Design and Chiral Polymer Synthesis*, John Wiley & Sons, Inc., Hoboken, New Jersey, **2011**.
- [2] Coates, G. W.; Waymouth, R. M. Enantioselective Cyclopolymerization of 1,5-Hexadiene Catalyzed by Chiral Zirconocenes: A Novel Strategy for the Synthesis of Optically Active Polymers with Chirality in the Main Chain. *J. Am. Chem. Soc.* **1993**, *115*, 91–98.
- [3] Coates, G. W. In *Comprehensive Asymmetric Catalysis*, Eds.: Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H., Springer, Berlin, Germany, **1999**, pp. 1329–1349.
- [4] Xu, G.; Mahmood, Q.; Lv, C.; Yang, R.; Zhou, L.; Wang, Q. Asymmetric Kinetic Resolution Polymerization. *Coord. Chem. Rev.* **2020**, *414*, 213296.
- [5] Nakano, T.; Okamoto, Y. Synthetic Helical Polymers: Conformation and Function. *Chem. Rev.* **2001**, *101*, 4013–4038.
- [6] Shen, J.; Okamoto, Y. Efficient Separation of Enantiomers Using Stereoregular Chiral Polymers. *Chem. Rev.* **2016**, *116*, 1094–1138.
- [7] Itsuno, S.; Paul, D. K.; Salam, M. A.; Haraguchi, N. Main-Chain Ionic Chiral Polymers: Synthesis of Optically Active Quaternary Ammonium Sulfonate Polymers and Their Application in Asymmetric Catalysis. *J. Am. Chem. Soc.* **2010**, *132*, 2864–2865.
- [8] Ciardelli, F.; Altomare, A.; Carlini, C. Chiral Discrimination in the Polymerization of α -Olefins by Ziegler-Natta Initiator Systems. *Prog. Polym. Sci.* **1991**, *16*, 259–277.
- [9] Ito, S.; Nozaki, K. In *Catalytic Asymmetric Synthesis*, 3rd ed., Ed.: Ojima, I., John Wiley & Sons, New York, **2010**, pp. 931–985.
- [10] Yamamoto, T.; Murakami, R.; Komatsu, S.; Sugimoto, M. Chirality-Amplifying, Dynamic Induction of Single-Handed Helix by Chiral Guests to Macromolecular Chiral Catalysts Bearing Boronyl Pendants as Receptor Sites. *J. Am. Chem. Soc.* **2018**, *140*, 3867–3870.
- [11] Chu, J.-H.; Xu, X.-H.; Kang, S.-M.; Liu, N.; Wu, Z.-Q. Fast Living Polymerization and Helix-Sense-Selective Polymerization of Diazoacetates Using Air-Stable Palladium(II) Catalysts. *J. Am. Chem. Soc.* **2018**, *140*, 17773–17781.
- [12] Nagata, Y.; Takeda, R.; Sugimoto, M. Asymmetric Catalysis in Chiral Solvents: Chirality Transfer with Amplification of Homochirality through a Helical Macromolecular Scaffold. *ACS Cent. Sci.* **2019**, *5*, 1235–1240.
- [13] Brookhart, M.; Wagner, M. I.; Balavoine, G. G. A.; Haddou, H. A. Polymers with Main-Chain Chirality. Synthesis of Highly Isotactic, Optically Active Poly(4-tert-butylstyrene-alt-CO) Using Pd(II) Catalysts Based on C₂-Symmetric Bisoxazoline Ligands. *J. Am. Chem. Soc.* **1994**, *116*, 3641–3642.
- [14] Jiang, Z. Z.; Sen, A. Palladium(II)-Catalyzed Isospecific Alternating Copolymerization of Aliphatic α -Olefins with Carbon Monoxide and Isospecific Alternating Isomerization Cooligo-merization of a 1,2-Disubstituted Olefin with Carbon Monoxide. Synthesis of Novel, Optically Active, Isotactic 1,4- and 1,5-Polyketones. *J. Am. Chem. Soc.* **1995**, *117*, 4455–4467.
- [15] Nozaki, K.; Sato, N.; Takaya, H. Highly Enantioselective Alternating Copolymerization of Propene with Carbon Monoxide Catalyzed by a Chiral Phosphine-Phosphite-Palladium(II) Complex. *J. Am. Chem. Soc.* **1995**, *117*, 9911–9912.
- [16] Kosaka, N.; Nozaki, K.; Hiyama, T.; Fujiki, M.; Tamai, N.; Matsumoto, T. Conformational Studies on an Optically Active 1,4-Polyketone in Solution. *Macromolecules* **2003**, *36*, 6884–6887.
- [17] Nakano, K.; Nozaki, K.; Hiyama, T. Asymmetric Alternating Copoly-

- merization of Cyclohexene Oxide and CO₂ with Dimeric Zinc Complexes. *J. Am. Chem. Soc.* **2003**, *125*, 5501–5510.
- [18] Nakano, K.; Hashimoto, S.; Nakamura, M.; Kamada, T.; Nozaki, K. Stereocomplex of Poly(propylene carbonate): Synthesis of Stereogradient Poly(propylene carbonate) by Regio- and Enantioselective Copolymerization of Propylene Oxide with Carbon Dioxide. *Angew. Chem. Int. Ed.* **2011**, *50*, 4868–4871.
- [19] Kamahori, K.; Tada, S.; Ito, K.; Itsuno, S. Optically Active Polymer Synthesis by Diels-Alder Polymerization with Chirally Modified Lewis Acid Catalyst. *Macromolecules* **1999**, *32*, 541–547.
- [20] Kumagai, T.; Itsuno, S. Asymmetric Polymerization of Dialdehyde and Bis(allylsilane) in the Presence of Chiral (Acyloxy)borane Catalyst. *Macromolecules* **2001**, *34*, 7624–7628.
- [21] Itsuno, S. Chiral Polymer Synthesis by Means of Repeated Asymmetric Reaction. *Prog. Polym. Sci.* **2005**, *30*, 540–558.
- [22] Nagai, D.; Sudo, A.; Endo, T. Anionic Alternating Copolymerization of Ketene and Aldehyde: Control of Enantioselectivity by Bisoxazoline-type Ligand for Synthesis of Optically Active Polyesters. *Macromolecules* **2006**, *39*, 8898–8900.
- [23] Uno, T.; Ohta, H.; Yamane, A.; Kubo, M.; Itoh, T. Synthesis and Asymmetric Anionic Polymerization of Substituted 7-Aryl-2,6-dimethyl-1,4-benzoquinone Methides. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 437–444.
- [24] Onimura, K.; Tsutsumi, H.; Oishi, T. Asymmetric Anionic Polymerization of N-Substituted Maleimides with *n*-Butyllithium-methylene-bridged 2,2-Bis(oxazoline) Complexes. *Macromolecules* **1998**, *31*, 5971–5976.
- [25] Isobe, Y.; Onimura, K.; Tsutsumi, H.; Oishi, T. Asymmetric Polymerization of *N*-1-Naphthylmaleimide with Chiral Anionic Initiator: Preparation of Highly Optically Active Poly(*N*-1-naphthyl-maleimide). *Macromolecules* **2001**, *34*, 7617–7623.
- [26] Nakano, T.; Yade, T.; Okamoto, Y. Revised Interpretation for *N*-Cyclohexylmaleimide Polymerization in the Presence of an Optically Active Cobalt(II) Complex: Polymerization Mediated by Anionic Species Formed through Monomer-Co(II) Complex-O₂ Interaction. *Macromolecules* **2003**, *36*, 3498–3504.
- [27] Kanbayashi, N.; Okamura, T.; Onitsuka, K. New Method for Asymmetric Polymerization: Asymmetric Allylic Substitution Catalyzed by a Planar-Chiral Ruthenium Complex. *Macromolecules* **2014**, *47*, 4178–4185.
- [28] Kanbayashi, N.; Hosoda, K.; Okamura, T.; Aoshima, S.; Onitsuka, K. Enantio- and Diastereoselective Polymerization: Asymmetric Allylic Alkylation Catalyzed by a Planar-chiral Cp^{*}Ru Complex. *Polym. Chem.* **2016**, *7*, 3691–3699.
- [29] Kanbayashi, N.; Okamura, T.; Onitsuka, K. New Synthetic Approach for Optically Active Polymer Bearing Chiral Cyclic Architecture: Combination of Asymmetric Allylic Amidation and Ring-closing Metathesis Reaction. *Macromolecules* **2015**, *48*, 8437–8444.
- [30] Zhou, L.; Xu, X.-H.; Jiang, Z.-Q.; Xu, L.; Chu, B.-F.; Liu, N.; Wu, Z.-Q. Selective Synthesis of Single-Handed Helical Polymers from Achiral Monomer and a Mechanism Study on Helix-Sense-Selective Polymerization. *Angew. Chem. Int. Ed.* **2021**, *60*, 806–812.
- [31] Liu, W.-B.; Xu, X.-H.; Kang, S.-M.; Song, X.; Zhou, L.; Liu, N.; Wu, Z.-Q. Bottlebrush Polymers Carrying Side Chains on Every Backbone Atom: Controlled Synthesis, Polymerization-Induced Emission, and Circularly Polarized Luminescence. *Macromolecules* **2021**, *54*, 3158–3168.
- [32] Lu, X.-B.; Darensbourg, D. J. Cobalt Catalysts for the Coupling of CO₂ and Epoxides to Provide Polycarbonates and Cyclic Carbonates. *Chem. Soc. Rev.* **2012**, *41*, 1462–1484.
- [33] Childers, M. I.; Longo, J. M.; Zee, N. J. V.; LaPointe, A. M.; Coates, G. W. Stereoselective Epoxide Polymerization and Copolymerization. *Chem. Rev.* **2014**, *114*, 8129–8152.
- [34] Li, J.; Ren, B.-H.; Wan, Z.-Q.; Chen, S.-Y.; Liu, Y.; Ren, W.-M.; Lu, X.-B. Enantioselective Resolution Copolymerization of Racemic Epoxides and Anhydrides: Efficient Approach for Stereoregular Polyesters and Chiral Epoxides. *J. Am. Chem. Soc.* **2019**, *141*, 8937–8942.
- [35] Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, Wiley, New York, **1998**.
- [36] Ford, A.; Miel, H.; Ring, A.; Slattery, C. N.; Maguire, A. R.; McKervey, M. A. *Modern Organic Synthesis with α -Diazocarbonyl Compounds*. *Chem. Rev.* **2015**, *115*, 9981–10080.
- [37] Xia, Y.; Qiu, D.; Wang, J. Transition-Metal-Catalyzed Cross-Couplings through Carbene Migratory Insertion. *Chem. Rev.* **2017**, *117*, 13810–13889.
- [38] Zhu, S.-F.; Zhou, Q.-L. Iron-catalyzed Transformations of Diazo Compounds. *Natl. Sci. Rev.* **2014**, *1*, 580–603.
- [39] Ren, Y.-Y.; Zhu, S.-F.; Zhou, Q.-L. Chiral Proton-transfer Shuttle Catalysts for Carbene Insertion Reactions. *Org. Biomol. Chem.* **2018**, *16*, 3087–3094.
- [40] Zhu, S.-F.; Zhou, Q.-L. Transition-Metal-Catalyzed Enantioselective Heteroatom-Hydrogen Bond Insertion Reactions. *Acc. Chem. Res.* **2012**, *45*, 1365–1377.
- [41] Ihara, E.; Saiki, K.; Goto, Y.; Itoh, T.; Inoue, K. Polycondensation of Bis(diazocarbonyl) Compounds with Aromatic Diols and Cyclic Ethers: Synthesis of New Type of Polyetherketones. *Macromolecules* **2010**, *43*, 4589–4598.
- [42] Ihara, E.; Hara, Y.; Itoh, T.; Inoue, K. Three-Component Polycondensation of Bis(diazoketone) with Dicarboxylic Acids and Cyclic Ethers: Synthesis of New Types of Poly(ester ether ketone)s. *Macromolecules* **2011**, *44*, 5955–5960.
- [43] Zhu, J.-B.; Watson, E. M.; Tang, J.; Chen, E. Y.-X. A Synthetic Polymer System with Repeatable Chemical Recyclability. *Science* **2018**, *360*, 398–403.
- [44] Tang, X.; Westlie, A. H.; Watson, E. M.; Chen, E. Y.-X. Stereo-sequenced Crystalline Polyhydroxyalkanoates from Diastereomeric Monomer Mixtures. *Science* **2019**, *366*, 754–758.
- [45] Wang, X.; Ding, Y.; Tao, Y.; Wang, Z.; Wang, Z.; Yan, J. Polycondensation of Bis(α -diazo-1,3-dicarbonyl) Compounds with Dicarboxylic Acids: An Efficient Access to Functionalized Alternating Polyesters. *Polym. Chem.* **2020**, *11*, 1708–1712.
- [46] Shimomoto, H.; Mukai, H.; Bekku, H.; Itoh, T.; Ihara, E. Ru-Catalyzed Polycondensation of Dialkyl 1,4-Phenylenebis-(diazoacetate) with Dianiline: Synthesis of Well-Defined Aromatic Polyamines Bearing an Alkoxy-carbonyl Group at the Adjacent Carbon of Each Nitrogen in the Main Chain Framework. *Macromolecules* **2017**, *50*, 9233–9238.
- [47] Buck, R. T.; Doyle, M. P.; Drysdale, M. J.; Ferris, L.; Forbes, D. C.; Haigh, D.; Moody, C. J.; Pearson, N. D.; Zhou, Q.-L. Asymmetric Rhodium Carbenoid Insertion into the Si-H Bond. *Tetrahedron Lett.* **1996**, *37*, 7631–7634.
- [48] Davies, H. M. L.; Hansen, T.; Rutberg, J.; Bruzinski, P. R. Rhodium(II) (*S*)-*N*-(Arylsulfonyl)proline Catalyzed Asymmetric Insertions of Vinyl- and Phenylcarbenoids into the Si-H Bond. *Tetrahedron Lett.* **1997**, *38*, 1741–1744.
- [49] Ge, M.; Corey, E. J. A method for the Catalytic Enantioselective Synthesis of 6-Silylated 2-Cyclohexenones. *Tetrahedron Lett.* **2006**, *47*, 2319–2321.
- [50] Yang, L.-L.; Ouyang, J.; Zou, H.-N.; Zhu, S.-F.; Zhou, Q.-L. Enantioselective Insertion of Alkynyl Carbenes into Si-H Bonds: An Efficient Access to Chiral Propargylsilanes and Allenylsilanes. *J. Am. Chem. Soc.* **2021**, *143*, 6401–6406.
- [51] Zhang, Y.-Z.; Zhu, S.-F.; Wang, L.-X.; Zhou, Q.-L. Copper-Catalyzed Highly Enantioselective Carbenoid Insertion into Si-H Bonds. *Angew. Chem. Int. Ed.* **2008**, *47*, 8496–8498.
- [52] Zhai, X.-Y.; Hu, S.-B.; Shi, L.; Zhou, Y.-G. Synthesis of Poly(silyl ethers) via Iridium-Catalyzed Dehydrocoupling Polymerization. *Organometallics* **2018**, *37*, 2342–2347.
- [53] Zhai, X.-Y.; Wang, X.-Q.; Ding, Y.-X.; Zhou, Y.-G. Partially Biobased Polymers: The Synthesis of Polysilyl ethers via Dehydrocoupling Catalyzed by an Anionic Iridium Complex. *Chin. Chem. Lett.* **2020**, *31*,

1197–1200.

- [54] Zhai, X.-Y.; Wang, X.-Q.; Zhou, Y.-G. Cobalt-Catalyzed Selective Dehydrocoupling Polymerization of Prochiral Silanes and Diols. *Eur. Polym. J.* **2020**, *134*, 109832.
- [55] Wang, X.-Q.; Zhai, X.-Y.; Wu, B.; Bai, Y.-Q.; Zhou, Y.-G. Synthesis of Chiral Poly(silyl ether)s via CuH-Catalyzed Asymmetric Hydrosilylation Polymerization of Diketones with Silanes. *ACS Macro. Lett.* **2020**, *9*, 969–973.
- [56] Xie, X.-L.; Zhu, S.-F.; Guo, J.-X.; Cai, Y.; Zhou, Q.-L. Enantioselective

Palladium-Catalyzed Insertion of α -Aryl- α -diazoacetates into the O-H Bonds of Phenols. *Angew. Chem. Int. Ed.* **2014**, *53*, 2978–2981.

Manuscript received: August 08, 2021

Manuscript revised: September 19, 2021

Manuscript accepted: September 26, 2021

Accepted manuscript online: September 29, 2021

The Authors



Left to Right: Yong-Gui Zhou, Xiao-Qing Wang, Bo Wu, Xiao-Yong Zhai