

Synthesis of Poly(silyl ethers) via Iridium-Catalyzed Dehydrocoupling Polymerization

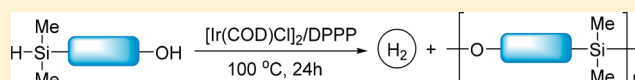
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Supporting Information

ABSTRACT: Poly(silyl ethers) (PSEs) are promising degradable materials, and the development of an efficient method to produce them from readily available materials is highly desirable. Herein, we present a dehydrocoupling polymerization of AB-type silyl alcohol monomers catalyzed by homogeneous iridium(I) complexes bearing a bisphosphine ligand. A series of PSEs containing aliphatic or aromatic linkers have been synthesized. The PDI of PSEs could be tuned by varying the ligand of iridium/bisphosphine complexes. Moderate to high yields of polymers with number-average molecular weights (M_n) up to 9.27×10^4 were obtained. The PSEs possess good thermal stability and low glass-transition temperature ($T_g = -42$ to -83 °C).



INTRODUCTION

Polymers containing silicon–oxygen bonds in the main chain, including polysiloxanes, poly(silyl ethers) (PSEs), poly(silyl esters), etc., possess analogous and intriguing properties: for instance, low T_g , good thermal stability, biocompatibility, and high gas permeability.^{1,2} These polymers have been applied in many fields, such as high-temperature elastomers,^{3a–c} conductive polymeric materials,^{3d} and chiral column packing materials.^{3e} As the result of main-chain hydrolytically degradable Si–O–C linkages, PSEs are promising degradable materials. More importantly, the degradability, thermal stability, and thermomechanical properties of PSEs can be conveniently adjusted by changing the structure of the monomers.⁴

Polycondensation of dichlorosilanes and diols is the most often used method to synthesize PSEs.⁵ However, dichlorosilanes are moisture-sensitive, which limits their further use. When dichlorosilanes were replaced with diphenoxy- and dianilinosilanes, polymers with high M_n were obtained at high reaction temperature.^{4a,b,6} Recently, acid-catalyzed silicon acetal metathesis polymerization (SAMP) further enriched the methodology of production of PSEs.⁷ However, HCl or other unwanted byproducts are not avoidable in polycondensation. To overcome this issue, polyaddition of dichlorosilanes with bis(epoxides) and bis(oxetanes) was developed, providing PSEs with good regioselectivity in the presence of quaternary ammonium under mild conditions.⁸ Usually, hydrosilylation polymerization of dicarbonyl compounds with dihydrosilanes can be realized by ruthenium-,^{4c,9} rhodium-,¹⁰ and zinc-based¹¹ catalytic systems. As an effective and highly atom-economical method to construct Si–O bonds, dehydrocoupling reactions of silanes and alcohols have been studied as the chain propagation of polymerization to synthesize PSEs with hydrogen gas as the only byproduct. Catalytic systems based

on palladium,^{4d,12,13} platinum,^{12a} rhodium,^{13,14} and manganese¹⁵ have been developed. Generally, the PSEs synthesized via metal-catalyzed cross-dehydrocoupling polymerization possess relatively lower M_n values in comparison to PSEs synthesized via ring-opening polymerization.¹⁶ Furthermore, boranes could also be used as effective metal-free catalysts in dehydrocoupling polymerization.¹⁷ Very recently, inorganic base cesium hydroxide catalyzed dehydrocoupling polymerization of a novel AB-type monomer was also reported by the Hartwig group.¹⁸ The degree of polymerization can be controlled by adding various amounts of the AA-type monomer 1,10-decanediol. Despite these advances, the further development of efficient strategies for the synthesis of high-molecular-weight PSEs containing various backbones is still meaningful.

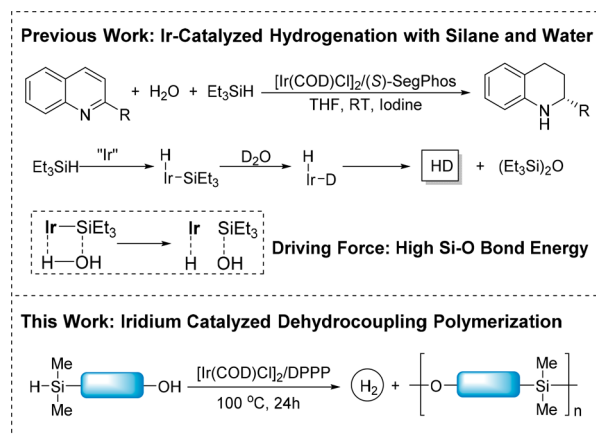
In transition-metal-catalyzed reactions, the ligand is of great importance in adjusting reactivity, chemoselectivity, regioselectivity, and enantioselectivity.¹⁹ Recently, we have investigated the performance of iridium/bisphosphine complexes in asymmetric hydrogenation.²⁰ In 2010, we found that an iridium/bisphosphine complex could effectively catalyze asymmetric hydrogenation of quinolines with triethylsilane and water as the hydrogen source,²¹ and a detailed mechanistic study indicated that the iridium complex could catalyze dehydrocoupling of triethylsilane and water to form hexaethylidisiloxane and hydrogen gas. We envisioned that the above iridium catalyst might be applied in synthesis of PSEs via the dehydrocoupling polymerization of silyl alcohol monomers. Iridium catalysts with different ligands should tune the M_n and PDI values of PSEs. To the best of our knowledge, homogeneous iridium catalysts have not been applied in the

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synthesis of PSEs via dehydrocoupling polymerization. Herein, we report the iridium/bisphosphine complex catalyzed dehydrocoupling polymerization of AB-type monomers bearing silane and alcohol moieties to give high-molecular-weight PSEs (Scheme 1).

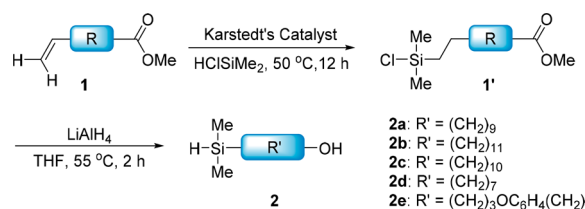
Scheme 1. Catalytic Dehydrocoupling Polymerization



RESULTS AND DISCUSSION

Synthesis of Monomers. Monomers **2a–e** could be conveniently synthesized via two steps (Scheme 2).¹⁸ The first step is hydrosilylation catalyzed by Karstedt's catalyst, followed by reduction using lithium aluminum hydride to give the desirable monomers.

Scheme 2. Synthesis of Monomers



Optimization of Conditions. 9-(Dimethylsilyl)nonan-1-ol (**2a**) was chosen as the model monomer to conduct the optimization of conditions. The results are depicted in Table 1. When $[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.5 mol %) was used as the catalyst, it was easy to observe that gases bubbled up. After 24 h, the product was purified by precipitation; the number-average molecular weight (M_n) of the polymer was not satisfactory. Only a low- M_n product was obtained ($M_n = 2900$, PDI = 1.23) (entry 1). To improve the molecular weight, the effect of the phosphine ligand was investigated. To our disappointment, a polymer with lower M_n value (1900) was obtained (entry 2) in the presence of PPh_3 . Afterward, the monophosphine PPh_3 was replaced with the bisphosphine DPPE. To our delight, a high-molecular-weight polymer with an M_n value of 49100 was obtained. This suggested that the catalytic performance of the iridium/bisphosphine complex is superior to that of the iridium/monophosphine complex (entry 3). However, the PDI of the polymer was not satisfactory (PDI = 5.74). Thus, a series of commercially available bisphosphine ligands were screened. The PDI of the polymer became gradually narrower on extending the chain length of the bisphosphine ligands

Table 1. Optimization of Conditions^a

entry	ligand	M_n^b	PDI ^b	yield (%) ^c
1		2900	1.23	n.d.
2 ^d	PPh_3	1300	1.08	n.d.
3	DPPE	49100	5.74	92
4	DPPP	92700	3.70	79
5	DPPB	70200	3.17	87
6	DCPE	67000	2.11	80
7	DPPF	76400	2.05	81

^aReaction conditions unless specified otherwise: **2a** (1 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.5 mol %), ligand (1 mol %), neat, 100 °C, 24 h.

^bDetermined by GPC with RI. ^cIsolated yield; n.d. = not detected.

^dLigand (2 mol %).

(entries 3–5). A polymer with narrower PDI could be obtained by using electron-rich and highly sterically hindered ligands (DPPF and DCPE) (entries 6 and 7). Through condition optimization, the highest M_n value of 92700 and PDI of 2.05 could be obtained by using DPPP and ferrocene-derived DPPF, respectively (entry 4 and entry 7). In consideration of the M_n value of PSE, we chose $[\text{Ir}(\text{COD})\text{Cl}]_2/\text{DPPP}$ as the best catalyst.

Next, the effects of reaction temperature, solvent, and metal precursor were conducted. The results are depicted in Table 2.

Table 2. Further Optimization of Conditions^a

entry	T (°C)	solvent	M_n^b	PDI ^b	yield (%) ^c
1	40	neat	4100	1.30	47
2	60	neat	20500	1.68	92
3	80	neat	37500	2.08	50
4	100	neat	92700	3.70	79
5	120	neat	62000	3.73	gel
6 ^d	100	DCE			
7 ^d	100	dioxane			
8 ^d	100	CH_3CN	12900	1.73	42
9 ^d	100	toluene	32400	1.57	47
10 ^e	100	toluene	42900	3.10	91
11 ^f	100	neat			

^aReaction conditions unless specified otherwise: **2a** (1 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.5 mol %), DPPP (1 mol %), 100 °C, 24 h.

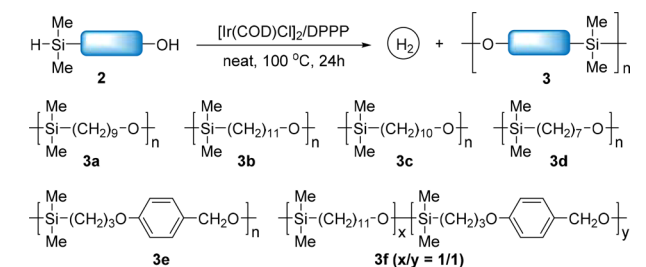
^bDetermined by GPC with RI. ^cIsolated yield. ^dSolvent used was 3 mL. ^eToluene used was 1 mL. ^f $[\text{Ir}(\text{COD})\text{Cl}]_2$ was replaced with $[\text{Ir}(\text{COD})\text{OMe}]_2$.

Lowering the temperature resulted in an apparent decrease of M_n (entries 1–3). However, when the temperature was raised to 120 °C, a gel with poor solubility in common organic solvents was obtained (entry 5), which is not the target product. Then, the solvent effects were examined. Unfortunately, no product was obtained in 1,2-dichloroethane (DCE)

or dioxane (entries 6 and 7). Although good PDI values were obtained in CH₃CN and toluene, the M_n and yield were not ideal (entries 8 and 9). In order to achieve high M_n and narrow PDI, the solvent was reduced to 1.0 mL. However, poor PDI was observed (entry 10). When [Ir(COD)Cl]₂ was replaced with [Ir(COD)OMe]₂, no reaction took place (entry 11). This suggested that the coordinated anion of the metal precursor has a prominent influence on polymerization. Therefore, the optimal reaction conditions were finally established as [Ir(COD)Cl]₂/DPPP/neat/100 °C/24 h.

Substrate Scope. With the optimal conditions in hand, the generality of the dehydrocoupling polymerization was investigated (Table 3). For the monomers containing aliphatic

Table 3. Substrate Scope: Monomers Containing Aliphatic and Aromatic Backbones^a



entry	monomer	M_n^b	PDI ^b	yield (%) ^c
1	2a	92700	3.70	79 (3a)
2	2b	46900	2.90	80 (3b)
3	2c	25500	2.55	98 (3c)
4	2d	30500	2.39	96 (3d)
5	2e	20800	1.71	75 (3e)
6 ^d	2b + 2e	15000	1.89	78 (3f)

^aReaction conditions unless specified otherwise: 2a–e (1 mmol), [Ir(COD)Cl]₂ (0.5 mol %), DPPP (1 mol %), neat, 100 °C, 24 h. ^bDetermined by GPC with RI. ^cIsolated yield. ^d2b (0.5 mmol) and 2e (0.5 mmol) were used.

backbones, dehydrocoupling polymerization proceeded smoothly (entries 1–4). The M_n value of PSE 3b is close to the value reported for cesium hydroxide catalyzed dehydrocoupling polymerization ($M_n = 49000$ vs 46900).¹⁸ For monomers containing aromatic backbones (entry 5), the dehydrocoupling polymerization also proceeded smoothly with an M_n value of 20800 and slightly better PDI value of 1.71. In order to make this strategy more versatile, the copolymerization of monomers 2b and 2e was conducted. To our delight, the desired product was obtained with an M_n value of 15000 and PDI value of 1.89 (entry 6). Because monomer 2b can randomly react with itself or monomer 2e, the ratio of fragments of monomers 2b and 2e in polymer chain is 1:1.

Thermal Analysis. After purification by precipitation, the PSEs produced by the Ir-catalyzed dehydrocoupling polymerization were, in general, colorless/faint yellow viscous oils/soft solids, depending on the molar masses and backbones of polymers. The thermal properties of these polymers were investigated under a nitrogen atmosphere using TGA and DSC (Table 4). For chainlike polymers, T_{50} values of 3a–d were kept at around 470 °C, which indicated that these polymers all exhibit good thermal stability (entries 1–4). However, the T_5 values of chainlike polymers were quite different (from 350 to 422 °C). Relatively speaking, copolymerization product 3f and polymer 3e containing an aromatic backbone were more likely

Table 4. Thermal Analysis of Polymers^a

entry	PSE	T_5 (°C) ^a	T_{50} (°C) ^a	T_g (°C) ^b
1	3a	422	471	−75.6
2	3b	421	469	−83.2
3	3c	350	466	n.o.
4	3d	375	467	n.o.
5	3e	324	412	−42.1
6	3f	296	434	n.o.

^aTemperature at which 5% and 50% mass loss are observed under N₂ by TGA. ^bDetermined by DSC; n.o. = not observed.

to suffer pyrolysis (entries 5 and 6). Thus, these PSEs have thermal stabilities similar to those of PSEs synthesized via hydrosilylation.²² For polymers 3a,b, low glass transition temperatures (around −80 °C) could be detected (entries 1 and 2). However, polymers 3c,d,f exhibited an indiscernible glass transition via DSC (entries 3, 4, and 6). For polymer 3e containing an aromatic backbone, the T_g value was higher than that of polymers containing aliphatic backbones (entry 5). This indicated that incorporating aromatic groups in the main chain of the polymer might increase the barrier of longitudinal motion of the polymer chains.²³

Methanolysis. The degradability of polymer 3e was examined in a THF/methanol mixture at room temperature (Figure 1). The change in the M_n value of polymer 3e was

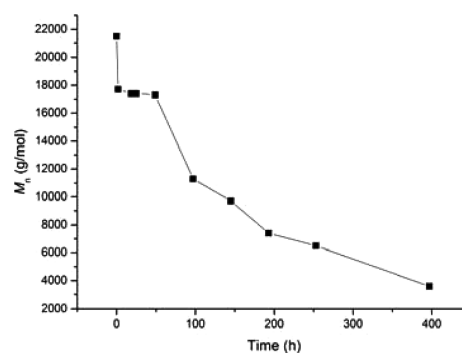


Figure 1. Degradation behavior of polymers in a THF/methanol mixture (80/20, v/v) at room temperature.

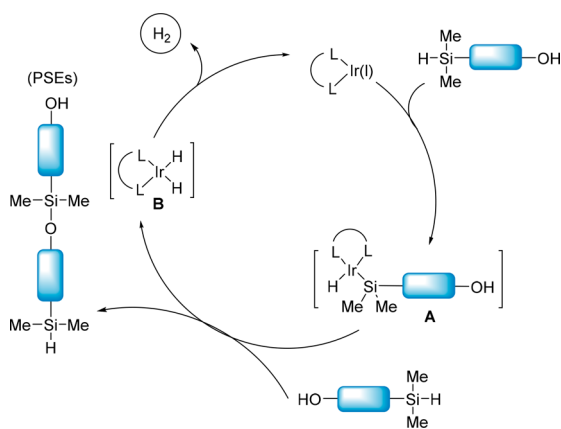
monitored by GPC. As shown in Figure 1, the M_n value of the polymer dropped quickly from 21500 to 17700 in 2 h. Then, the M_n value of the polymer decreased to 3600 within 242 h via slow degradation.

Plausible Mechanism. On the basis of these results and early studies,²⁴ a plausible mechanism is proposed for the iridium-catalyzed dehydrocoupling polymerization of an AB-type monomer (Scheme 3). First, iridium hydride intermediate A is formed via oxidative addition of the Si–H bond to the iridium(I) species. Then, intermediate A undergoes direct nucleophilic attack of another monomer at the coordinated silicon to furnish the dehydrocoupling product and intermediate B. Finally, reductive elimination of intermediate B provides hydrogen gas and regenerates iridium(I) species to complete the catalytic cycle.

SUMMARY

In conclusion, we have demonstrated that an iridium/bisphosphine complex can effectively catalyze dehydrocoupling polymerization for the synthesis of various PSEs from AB-type monomers. For the monomers containing aliphatic and

Scheme 3. Possible Mechanism for Ir-Catalyzed Dehydrocoupling Polymerization

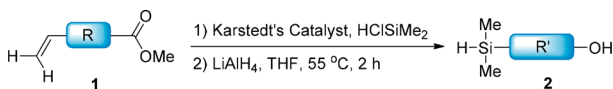


aromatic backbones, dehydrocoupling polymerization could occur; moderate to high yields of polymers and number-average molecular weights of up to 9.27×10^4 were obtained. The PSEs possess good thermal stability and low glass-transition temperature ($T_g = -42$ to -83 °C). Further work will focus on improving the PDI of polymers and synthesis of optically active PSEs.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques, unless otherwise noted. Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. ^1H NMR and ^{13}C NMR spectra were recorded at room temperature in CDCl_3 on 400 MHz instrument with tetramethylsilane (TMS) as internal standard. Flash column chromatography was performed on silica gel (200–300 mesh). GPC was performed on a Waters 1515 chromatography system equipped with an Agilent PL1110 column using THF as the eluent (35 °C, 1 mL/min). Polystyrene standards were used for calibration. DSC was performed on a DSC Instruments 204 HP calorimeter (purge gas, N_2 ; flow rate, 20 mL/min; ramp rate, 10 °C/min; temperature range, -100 to $+300$ °C). TGA was performed on a STA Instruments 449 F3 thermogravimetric analyzer under nitrogen from 25 to 600 °C at a ramp rate of 10 °C/min.

Preparation of Monomers. Monomers **2a–e** were conveniently prepared according to the literature method.¹⁸ Monomer **2b** is a known compound, and its NMR data matched the literature data.¹⁸



To a mixture of chlorodimethylsilane (7.896 g, 86 mmol) and **1** (72 mmol) in a 125 mL sealed tube was added Karstedt's catalyst ($\sim 2\%$ xylene solution, 7 μL , 0.001 mol %). The tube was heated under nitrogen at 50 °C for 12 h. After the tube was cooled to room temperature, the contents of the flask were added dropwise to a stirred suspension of LiAlH_4 (4.819 g, 129 mmol) in dry THF (350 mL) in an oven-dried 1 L flask under nitrogen at 0 °C. The flask was shaken by hand occasionally to break up the chunks that formed. After the addition of the chlorosilane intermediate, the flask was heated at 55 °C for 2 h before it was cooled to 0 °C. The reaction mixture was quenched by slow addition of ethyl acetate (80 mL). To the mixture was added dropwise an aqueous solution of Rochelle salt (40 g in 150 mL of water). The mixture was stirred vigorously. Then the aqueous layer was extracted with hexanes (100 mL \times 2). The combined organic layers were washed with water (100 mL \times 2) and brine (100 mL), dried over sodium sulfate, filtered, and concentrated

under reduced pressure. The residue was purified by silica gel column chromatography (50/1 to 20/1 hexanes/ethyl acetate) and then distilled to give monomer **2** as a colorless liquid. To improve the polymerization performance of monomers, an anhydration process was necessary to reduce the moisture content of monomers. Toluene (30 mL) and ethanol (7 mL) were added to monomer **2**, the azeotropic solvent was evaporated by fractional distillation, and the mixture was distilled under reduced pressure to obtain anhydrous monomer **2** as a colorless liquid.

9-(Dimethylsilyl)nonan-1-ol (2a): 90 mmol scale, 4.049 g, 22% overall yield, colorless liquid, new compound, $R_f = 0.24$ (hexanes/ethyl acetate = 10/1). ^1H NMR (400 MHz, CDCl_3): δ 3.87–3.79 (m, 1H), 3.63 (t, $J = 6.6$ Hz, 2H), 1.62–1.50 (m, 2H), 1.41–1.27 (m, 13H), 0.63–0.50 (m, 2H), 0.05 (d, $J = 3.7$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 63.3, 33.4, 33.0, 29.7, 29.6, 29.5, 25.9, 24.5, 14.3, -4.2 . HRMS-ESI: calcd for $\text{C}_{11}\text{H}_{25}\text{OSi}$ [$\text{M} - \text{H}$] $^+$, 201.1669; found 201.1670.

11-(Dimethylsilyl)undecan-1-ol (2b): 31 mmol scale, 2.200 g, 31% overall yield, colorless liquid, known compound, $R_f = 0.20$ (hexanes/ethyl acetate = 10/1). ^1H NMR (400 MHz, CDCl_3): δ 3.88–3.77 (m, 1H), 3.63 (t, $J = 6.6$ Hz, 2H), 1.62–1.51 (m, 2H), 1.38–1.25 (m, 17H), 0.61–0.53 (m, 2H), 0.05 (d, $J = 3.7$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 63.3, 33.4, 33.0, 29.8, 29.8, 29.63, 29.6, 25.9, 24.6, 14.4, -4.2 .

10-(Dimethylsilyl)decan-1-ol (2c): 72 mmol scale, 2.388 g, 15% overall yield, colorless liquid, new compound, $R_f = 0.34$ (hexanes/ethyl acetate = 10/1). ^1H NMR (400 MHz, CDCl_3): δ 3.87–3.78 (m, 1H), 3.63 (t, $J = 6.6$ Hz, 2H), 1.61–1.50 (m, 2H), 1.38–1.26 (m, 15H), 0.64–0.49 (m, 2H), 0.05 (d, $J = 3.7$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 63.3, 33.4, 33.0, 29.8, 29.7, 29.6, 29.5, 25.9, 24.6, 14.4, -4.2 . HRMS-ESI: calcd for $\text{C}_{12}\text{H}_{27}\text{OSi}$ [$\text{M} - \text{H}$] $^+$, 215.1826; found, 215.1825.

7-(Dimethylsilyl)heptan-1-ol (2d): 142 mmol scale, 3.516 g, 14% overall yield, colorless liquid, new compound, $R_f = 0.27$ (hexanes/ethyl acetate = 10/1). ^1H NMR (400 MHz, CDCl_3): δ 3.87–3.78 (m, 1H), 3.63 (t, $J = 6.6$ Hz, 2H), 1.62–1.50 (m, 2H), 1.37–1.30 (m, 9H), 0.64–0.52 (m, 2H), 0.05 (d, $J = 3.7$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 63.3, 33.3, 33.0, 29.3, 25.9, 24.5, 14.3, -4.2 . HRMS-ESI: calcd for $\text{C}_9\text{H}_{21}\text{OSi}$ [$\text{M} - \text{H}$] $^+$, 173.1356; found, 173.1359.

4-(3-(Dimethylsilyl)propoxy)phenylmethanol (2e): 95 mmol scale, 5.770 g, 27% overall yield, colorless liquid, new compound, $R_f = 0.19$ (hexanes/ethyl acetate = 10/1). ^1H NMR (400 MHz, CDCl_3): δ 7.27 (d, $J = 8.6$ Hz, 2H), 6.88 (d, $J = 8.6$ Hz, 2H), 4.60 (s, 2H), 3.87–3.95 (m, 3H), 1.89–1.77 (m, 2H), 1.67–1.60 (br, 1H), 0.76–0.66 (m, 2H), 0.11 (d, $J = 3.7$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 158.9, 133.1, 128.8, 114.8, 70.5, 65.3, 24.4, 10.5, -4.3 . HRMS-ESI: calcd for $\text{C}_{12}\text{H}_{19}\text{O}_2\text{Si}$ [$\text{M} - \text{H}$] $^+$, 223.1149; found, 223.1147.

General Procedure for the Polymerization. In an oven-dried 25 mL resealable Schlenk flask equipped with a magnetic stir bar were charged DPPP (4.2 mg, 0.01 mmol), $[\text{Ir}(\text{COD})\text{Cl}]_2$ (3.4 mg, 0.005 mmol), and DCM (3 mL) under nitrogen. The solution was stirred at room temperature for 10 min. Then the solvent was removed under reduced pressure to prepare the catalyst in situ. Monomer **2** (1 mmol) was placed in the flask under nitrogen. The flask was heated at 100 °C for 24 h under nitrogen (connected to an N_2 Schlenk line). During the last 6 h of the reaction time, H_2 produced during the reaction was replaced with N_2 every 2 h. After the polymerization, the reaction mixture was cooled to room temperature, and the contents was purified by a precipitation method.

All of the polymers are soluble in tetrahydrofuran and insoluble in methanol. Therefore, these two solvents were used in the precipitation process. The reaction mixture was first homogenized by the addition of an as low as possible amount of THF (1–2 mL), and then cold methanol was added portionwise (15–20 mL) until a change occurred to a biphasic mixture. The top layer was taken out, and the bottom viscous/solid layer was washed with MeOH two times until it gave a white/light yellow color viscous/solid polymer. The resulting polymer was dried to a constant weight and characterized by ^1H NMR, ^{13}C NMR, GPC, TG, and DSC.

Polymer 3a: colorless soft solid (0.158 g, 79% yield). ^1H NMR (400 MHz, CDCl_3): δ 3.56 (t, $J = 6.7$ Hz, 2H), 1.57–1.45 (m, 2H), 1.35–1.24 (m, 12H), 0.64–0.50 (m, 2H), 0.07 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 63.0, 33.7, 33.0, 29.8, 29.7, 29.5, 26.1, 23.4, 16.6, –1.9.

Polymer 3b: colorless soft solid (0.183 g, 80% yield). ^1H NMR (400 MHz, CDCl_3): δ 3.56 (t, $J = 6.7$ Hz, 2H), 1.57–1.46 (m, 2H), 1.34–1.24 (m, 16H), 0.64–0.49 (m, 2H), 0.08 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 63.0, 33.7, 33.0, 29.9, 29.8, 29.7, 29.6, 26.1, 23.4, 16.6, –1.9.

Polymer 3c: colorless soft solid (0.210 g, 98% yield). ^1H NMR (400 MHz, CDCl_3): δ 3.56 (t, $J = 6.7$ Hz, 2H), 1.58–1.45 (m, 2H), 1.34–1.23 (m, 14H), 0.65–0.49 (m, 2H), 0.08 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 63.0, 33.7, 33.0, 29.9, 29.8, 29.7, 29.6, 26.1, 23.4, 16.6, –1.9.

Polymer 3d: colorless viscous oil (0.166 g, 96% yield). ^1H NMR (400 MHz, CDCl_3): δ 3.55 (t, $J = 6.7$ Hz, 2H), 1.56–1.44 (m, 2H), 1.34–1.26 (m, 8H), 0.62–0.51 (m, 2H), 0.07 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 63.0, 33.7, 33.0, 29.4, 26.0, 23.4, 16.5, –1.9.

Polymer 3e: light yellow solid (0.166 g, 75% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.22 (d, $J = 8.5$ Hz, 2H), 6.85 (d, $J = 8.5$ Hz, 2H), 4.64 (s, 2H), 3.90 (t, $J = 6.7$ Hz, 2H), 1.91–1.76 (m, 2H), 0.81–0.66 (m, 2H), 0.16 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 158.5, 133.0, 128.2, 114.5, 70.6, 64.7, 23.4, 12.6, –1.8.

Polymer 3f: light yellow oil (0.175 g, 78% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.26–7.19 (m, 2H), 6.90–6.81 (m, 2H), 4.62 (d, $J = 7.3$ Hz, 2H), 3.90 (dd, $J = 12.4, 6.4$ Hz, 2H), 3.57 (dd, $J = 14.7, 6.9$ Hz, 2H), 1.88–1.78 (m, 2H), 1.56–1.46 (m, 2H), 1.36–1.24 (m, 16H), 0.80–0.64 (m, 2H), 0.64–0.54 (m, 2H), 0.20–0.05 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3): δ 158.5, 133.2, 133.0, 129.6, 128.8, 128.2, 114.8, 114.5, 71.7, 70.6, 64.7, 64.6, 63.1, 63.0, 33.7, 33.0, 29.8, 29.7, 29.6, 26.0, 23.4, 18.6, 16.6, 14.5, 12.7, 12.6, 0.5, –0.1, –1.8, –1.9.

Methanolysis. In a 10 mL flask were placed the polymer (20 mg) and THF (2 mL). After the polymer dissolved completely, methanol (0.5 mL) was added to the solution. A small amount of the solution was taken for GPC analysis after stirring for a certain time.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.organomet.8b00316](https://doi.org/10.1021/acs.organomet.8b00316).

General procedures and NMR spectra of the obtained compounds (PDF)

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Notes

The authors declare no competing financial interest.

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