

The catalytic cleavage of carbon-carbon double bond in polychloroprene induced by Schwartz's reagent via chlorine self-assisted β -alkyl elimination mechanism

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HIGHLIGHTS

- Schwartz's reagent ($[\text{Cp}_2\text{ZrHCl}]_n$) could cleave carbon-carbon double bond in PCP.
- Chlorine self-assisted β -alkyl elimination reaction for PCP chain scission.
- Catalytic cleavage of PCP chain was achieved in the case of $[\text{Cp}_2\text{ZrHCl}]_n$ with LiH and H_2 .

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ABSTRACT

The carbon-carbon double bonds ($\text{C}=\text{C}$) in polychloroprene (PCP) was broken down by Schwartz's reagent ($[\text{Cp}_2\text{ZrClH}]_n$) under mild conditions. The reaction mechanism for cleaving $\text{C}=\text{C}$ bonds in PCP was studied in detail. It was found that the cleavage pathway was chlorine self-assisted β -alkyl elimination reaction, namely, β -alkyl elimination was promoted while chlorine in PCP was eliminated by releasing Cp_2ZrCl_2 . The molecular weights of chain-scission products were controlled ranging from starting molecular weights of PCP to 0.2 kg mol^{-1} ; at the same time, microstructures of chain-scission products were similar to chain structures of original PCP. In addition, chain-scission products could be chain-end functionalized by electrophiles quenching chain scission reaction. More importantly, efficient catalytic chain cleavage was achieved under the synergistic effect of $[\text{Cp}_2\text{ZrClH}]_n$ with both LiH and H_2 .

1. Introduction

When carbon-carbon double ($\text{C}=\text{C}$) bonds encounter transition metal complexes, in general, $\text{C}=\text{C}$ bonds will coordinate with transition metal to perform subsequent addition reactions, such as the hydrosilylation [1], hydroaminomethylation [2], hydrogenation [3] and polymerization [4,5] *etc.*, in which the coordination of $\text{C}=\text{C}$ bonds with transition metal does not induce the cleavage of $\text{C}=\text{C}$ bonds. To transition metal, the occurrence of inducing the cleavage of $\text{C}=\text{C}$ bonds is generally involved in the oxidation of transition metal oxides [6–11], the controllability of which is not satisfactory. To the best of our knowledge, the cleavage of $\text{C}=\text{C}$ bonds induced by the coordination of transition metal complexes is rarely reported [12], especially, in the case of $\text{C}=\text{C}$ bonds bearing halogen substituent owing to halogen generally poisoning transition metal complexes. To the cleavage of

$\text{C}=\text{C}$ bonds bearing halogen, even though robust olefin metathesis reaction, the scission and regeneration of $\text{C}=\text{C}$ bonds, is also tricky [13] until Hoveyda et al. realized the efficient metathesis of alkenyl halides using molybdenum species in 2016 [14].

Schwartz's reagent, $[\text{Cp}_2\text{ZrHCl}]_n$, as a powerful tool in organic synthesis, has been used widely to functionalize the unactivated alkene (alkyne) [15–19]. For example, halogen, hydroxyl, carboxyl, aldehyde and even new carbon-carbon bond *etc.* were introduced into the reaction substrate by means of electrophiles addition and transmetalation of carbon-zirconium bond. However, the cleavage of alkene induced by Schwartz's reagent was paid little attention. In published literature, only the research about Schwartz's reagent cleaving carbon-heteroatom bond was reported. Cénac et al. reported that hydrozirconation promoted ring opening of nitrogen-, oxygen-, or phosphorus-containing unsaturated five-membered rings [20]. Buchwald groups [21] and

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Gronowitz groups [22] reported respectively that hydrozirconation led to the cleavage of carbon-oxygen bond in acyclic vinyl ethers, such as vinyl ethyl ether and β -methoxy styrene. And Caulton et al. also reported that Schwartz's reagent induced the cleavage of carbon-fluorine bond in vinyl fluoride [23]. But, under the hydrozirconation, the cleavage of carbon-carbon bond in alkene was hardly reported [24,25].

In this work, we found that the $[\text{Cp}_2\text{ZrHCl}]_n$ could not only cleave carbon-chlorine bond in polychloroprene (PCP), but also break down the C=C bonds in PCP. At the same time, it was found that β -alkyl elimination reaction causing carbon-carbon bond cleavage was promoted via chlorine self-assisted manners, that is, chlorine in PCP would be eliminated in the form of Cp_2ZrCl_2 once C=C bonds in PCP proceeded hydrozirconation addition. PCP could be cleaved into end-functionalized oligomers with controlled molecular weights under mild conditions. More importantly, efficiently catalytic cleavage of C=C bonds in PCP is achieved in the combination of $[\text{Cp}_2\text{ZrClH}]_n$ with LiH and H_2 . We believe that this research will shed some light on the C=C bonds cleavage in organic synthesis and bring novel inspiration to recycle wasted polymers by organometallic catalysts.

2. Experimental section

2.1. Materials and general measurements

Solvent THF was distilled from sodium/potassium alloy with benzophenone before use. Cp_2ZrHCl was prepared according to published procedure [26] using diisobutyl aluminium hydride ($i\text{Bu}_2\text{AlH}$, 1 M in hexane). Bis(cyclopentadienyl) zirconium dichloride (Cp_2ZrCl_2 , 99%), 2,3-dichloro-1-propene (98%) and copper(I) iodide (CuI , 99.998%) was purchased from Alfa Aesar. Phenethylmagnesium chloride (1.0 M in THF) was purchased from Acros. Polychloroprene (PCP) was a commercial product from Dupont. 2-Chloro-5-phenyl-1-pentene (CPP) was synthesized by reaction between 2,3-dichloro-1-propene and phenethylmagnesium chloride. Nuclear magnetic resonance (NMR) spectra were performed on Bruker AVANCE 500 (500 MHz for ^1H NMR, 77 MHz for ^2H NMR in CHCl_3 using CDCl_3 as standards ($\delta_{\text{D}} = 7.26$ ppm), 125 MHz for ^{13}C NMR) spectrometers and Bruker AVANCE 400 (400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR). Relative molecular weight was determined by gel permeation chromatography (GPC) on TOSOH HLC 8220 GPC at 40 °C using THF as an eluent against linear polystyrene standards.

2.2. Preparation of CPP

CPP was synthesized according to the published literature [27]. Firstly, 2,3-dichloro-1-propene (1.0 g) was added to the THF (10 ml) suspension of CuI (0.096 g) at room temperature and stirred for 10 min. Then cooled to -40 °C, phenethylmagnesium chloride (11.3 ml, 1.0 M in THF) was added dropwise for 5 min. The reaction mixture was warmed slowly to room temperature and stirred for overnight. Finally, it was quenched with saturated aqueous solution of NH_4Cl , and extracted with Et_2O (10 ml \times 4). The combined organic extracts were dried (Na_2SO_4) and evaporated. The residue was dissolved in hexane, filtered through silica gel and the filtrate was evaporated under reduced pressure. The product (0.8 g) was used without further purification.

2.3. General PCP cleavage procedure

Under an inert atmosphere of argon using standard Schlenk line techniques or M-Braun glovebox, $[\text{Cp}_2\text{ZrHCl}]_n$ powder was added to THF solution of PCP, and stirred for 3 h at 60 °C, then quenched with acidified methanol. Chain-scission products were precipitated in methanol and dried in vacuum oven at 30 °C to a constant weight.

Table 1
The molecular weights and PDI of chain-scission products from PCP.

Entry ^a	$[\text{Zr}]/[\text{C}=\text{C}]^b$	NMR ^c (kg mol^{-1})	M_n^d (kg mol^{-1})	PDI ^d
1	0	–	109.9	2.14
2	0.05	–	12.8	1.95
3	0.1	5.9	3.5	1.88
4	0.3	2.3	1.9	1.44
5	0.5	1.7	1.2	1.61
6	1.0	0.8	0.4	1.54
7	2.0	–	0.2	1.50

^a Conditions: THF, 60 °C, 3 h.

^b Molar ratio of ZrH and the C=C bonds in PCP.

^c Calculated M_n by NMR spectroscopy.

^d From GPC versus polystyrene standards (Fig. S1).

2.4. Hydrozirconation procedure of CPP

The reaction procedure was the same as above PCP. However, purified procedure was as following: Products were extracted by hexane after removing the solvent THF under water aspirator pressure. Then, hexane was also removed under water aspirator pressure to obtain final products that were characterized directly by NMR spectroscopy.

3. Results and discussion

3.1. Controlled PCP chain scission by $[\text{Cp}_2\text{ZrHCl}]_n$

A designed amount of $[\text{Cp}_2\text{ZrHCl}]_n$ (ZrH) powder was added to THF solution of PCP and vigorously stirred for 3 h at 60 °C, then quenched with acidified methanol. The isolated products were characterized by GPC, and the results were summarized in Table 1. It can be seen that the molecular weight (M_n) of chain-scission products is decreased with the increase of ZrH loading, suggesting that the molecular weight of chain-scission products is much controlled by the loading of ZrH. The chain-scission product with 0.2 kg mol^{-1} was obtained when the molar ratio of added ZrH to C=C bonds in PCP was equal to 2.0 (entry 7 in Table 1), indicating that PCP could be nearly cleaved into oligomers composed of three 2-chloro-1,3-butadiene monomers. Besides, chain-scission products are relatively narrower distributed (PDI \approx 1.6), implying the chain-scission reaction is well controlled.

Next, the microstructures of chain-scission products are investigated in detail. From ^1H NMR measurement (Fig. 1), it can be seen that the microstructures of chain-scission products are very similar to that of starting PCP, that is to say, there are no side reactions happening to disturb the microstructures of PCP during chain scission. In organic synthesis, hydrozirconation of alkene is generally accompanied with a few hydrogenation side reactions of C=C bonds [22,28–30]. However, the characteristic signal of $-\text{CHCl}-$ [31] is not detected by ^1H NMR spectroscopy (Fig. 1b–d), indicating that the hydrogenation side reaction does not occur in the case of PCP chain scission. As shown in ^1H NMR (Fig. 1b), primary protonic signals of chain-scission products were still assigned to characteristic unit of PCP, $-\text{CH}_2\text{C}(\text{Cl})=\text{CHCH}_2-$, although there were three new peaks at $\delta_{\text{H}} = 1.65$, 1.26, and 0.89 ppm. These three peaks were assigned to chain-end groups $-\text{CH}=\text{CHCH}_3$ (Fig. S2), $-\text{CH}_2\text{CH}_3$, and $-\text{CH}_3$ (Fig. 1), respectively. In addition, chain-end functionalization of chain-scission products was obtained by iodine (I_2) as quenching reagents. As shown in Fig. 1d, three new characteristic peaks at $\delta_{\text{H}} = 3.19$, 1.83, and 1.41 ppm were assigned to $-\text{CH}_2\text{I}$, $-\text{CH}_2\text{CH}_2\text{I}$ and $-\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$, respectively. Their coupling relationship was further confirmed by ^1H ^1H COSY and HSQC NMR spectra (Figs. S3 and S4). In conclusion, the microstructures of chain-scission products are also much controlled during the chain scission.

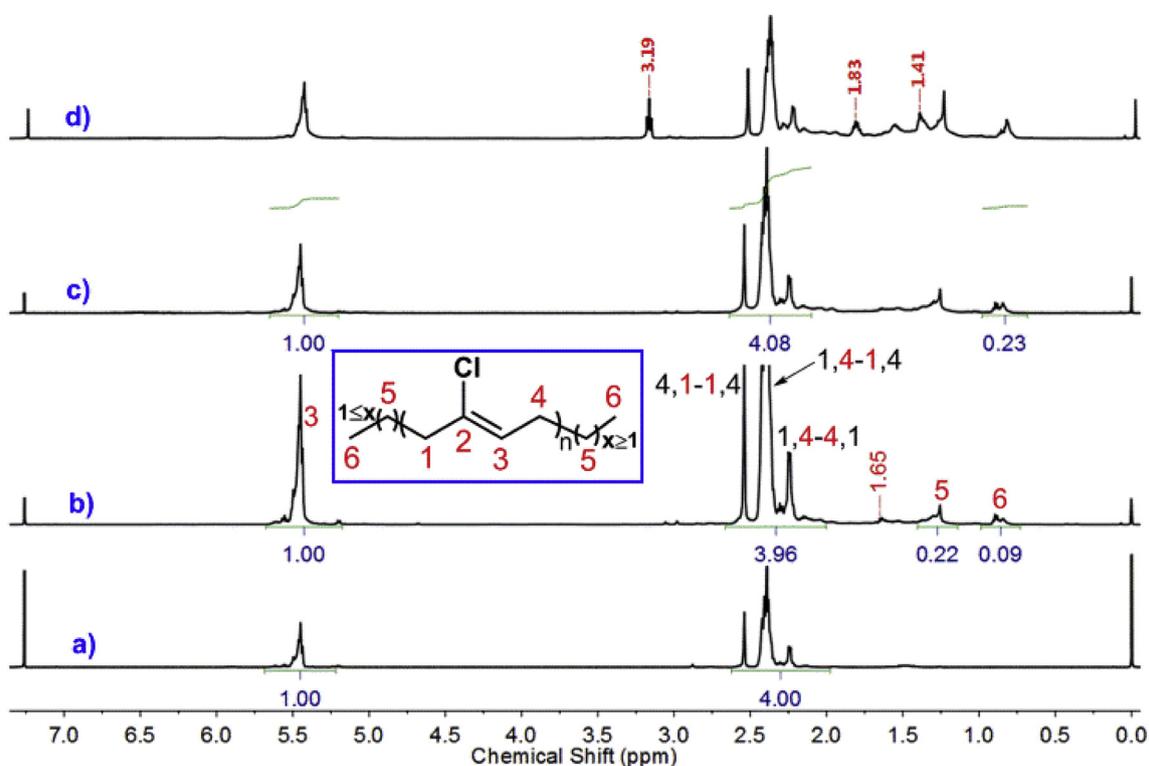
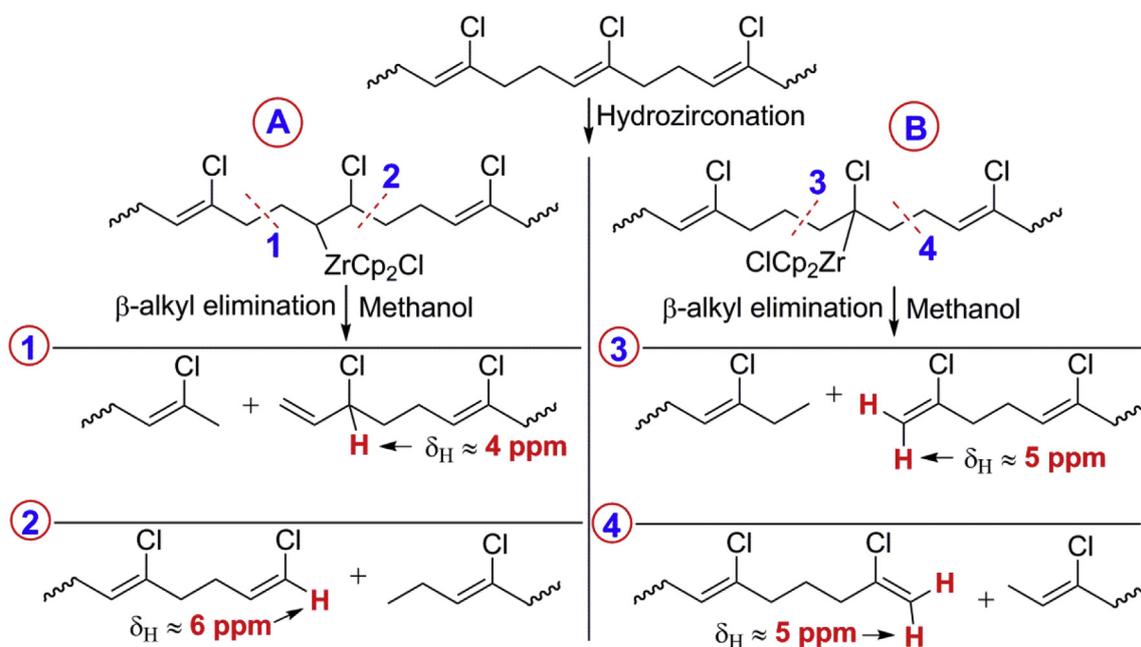


Fig. 1. ^1H NMR spectra of a) PCP; b-d) chain-scission products. (Conditions: THF, 60°C , 3 h; b) $[\text{Zr}]/[\text{C}=\text{C}] = 0.1$, acidified methanol quenched; c) $[\text{Zr}]/[\text{C}=\text{C}] = 0.3$, acidified methanol quenched; d) $[\text{Zr}]/[\text{C}=\text{C}] = 0.3$, I_2 quenched).

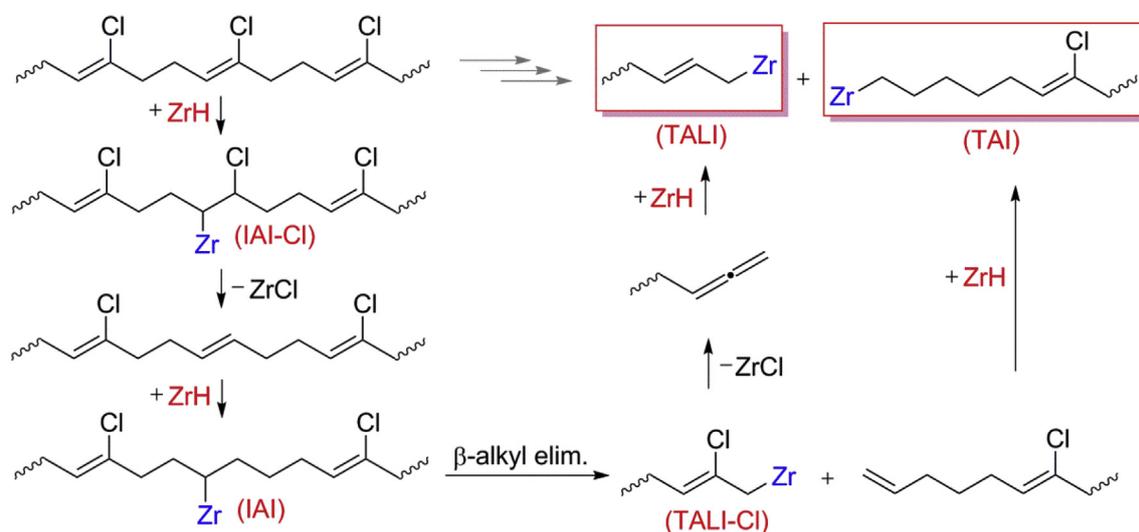
3.2. Chain scission mechanism in PCP

In our previous work [24], the proposed mechanism for ZrH inducing diene-based polymers chain scission is β -alkyl elimination. Hence, according to β -alkyl elimination mechanism, all of possible PCP chain scission pathways are depicted in Scheme 1. However, characteristic signals of generating chain end from all of chain scission pathways are not observed in ^1H NMR spectra (Fig. 1). According to the aforementioned analysis, the hydrogenation side reaction of $\text{C}=\text{C}$ bonds in PCP

chain scission does not take place, and the iodine chain-end functionalization, which is generated from electrophiles addition between chain-end alkylzirconium ($\text{C}-\text{Zr}$ bond) and I_2 , can be achieved. Accordingly, we deduce that the chlorine in PCP must be eliminated during chain scission. The chain scission mechanism involved in dechlorination is illustrated in Scheme 2. First of all, the regioselective hydrozirconation between PCP and ZrH gives an internal alkylzirconium intermediate bearing β -chloride substituent (IAI-Cl), in which zirconium is attached selectively to the chlorine-free substituted carbon



Scheme 1. Characteristic chain ends in PCP chain scission products via β -alkyl elimination without dechlorination.



Scheme 2. Proposed chain scission mechanism for PCP. (Zr = Cp₂ZrCl₂).

in C=C bonds [23]. Subsequently, zirconocene dichloride (Cp₂ZrCl₂) is eliminated owing to the existence of β-chlorine, in the meanwhile, internal C=C bonds without chlorine substituent are generated. Then, the further hydrozirconation of *in-situ* generated internal C=C bonds gives an IAI again, wherein PCP chain cleavage (C–C bond scission) is performed through β-alkyl elimination reaction, and two intermediates bearing two different chain ends are formed at the same time. One is the intermediate with chain-end C=C bonds and its further hydrozirconation will afford a relatively stable terminal alkylzirconation intermediate (TAI). And the other is terminal allylzirconium intermediate bearing a β-chlorine (TALI-Cl), hence, the elimination of chlorine will take place again in the form of Cp₂ZrCl₂ to afford an allene end. Under the hydrozirconation, allene end will be also turned into relatively stable TALI without a β-chlorine substituent.

To confirm the above proposed mechanism, it is critical to confirm the occurrence of twice dechlorination. All of first, to confirm the second dechlorination in Scheme 2, the valid method is to demonstrate the existence of allene intermediate. As aforementioned (Fig. 1b), the doublet of doublets at δ_H = 1.65 ppm (dd, ⁴J_{H-H} = 7 Hz) are assigned to –CH=CHCH₃ (Fig. S2), generated from methanol quenched the hydrozirconation intermediate of allene as shown in Scheme 2, indirectly implying that allene is possible to be formed during chain scission. Besides, using D₂O quenching the chain scission reaction, then the deuterium in chain-scission products was traced by ²H NMR spectroscopy. As is evidenced in Fig. 2, there is a small peak at δ_D = 5.47 ppm, assignment to the deuterium signal of –CH=CDCH₃. It is speculated that a few allene intermediate was hydrozirconated into internal alkenylzirconium species (–CH=C(ZrCp₂Cl)CH₃) rather than TALI [32], in this case, –CH=CDCH₃ chain end will be formed via D₂O quenching internal alkenylzirconium species. The above two indirect pieces of evidence proved that allene intermediate really exists. To detect direct evidence of allene intermediate, the ¹³C NMR spectroscopy was utilized since the characteristic signal of quaternary carbon in allene would appear around δ_C = 210 ppm [32,33]. In Fig. S5, a very weak peak at δ_C = 210.6 ppm is observed, further indicating that the allene

intermediate is generated during chain scission. From the above results, the second dechlorination in Scheme 2 is confirmed.

3.3. Evidence of eliminating Cp₂ZrCl₂ in the model compound CPP during the hydrozirconation

To the evidence of the first dechlorination in Scheme 2, however, taking into consideration about the complexity of polymer system, thus, we synthesized a model compound, 2-chloro-5-phenyl-1-pentene (CPP), to clarify the occurrence of the first Cp₂ZrCl₂ eliminating in the course of PCP chain scission. When the molar ratio of ZrH vs CPP was equal to 1.1, it can be seen from ¹H NMR spectra (Fig. 3b) that CPP was not thoroughly consumed under the hydrozirconation. And, the product from quenching hydrozirconation intermediate of CPP by methanol ((4-chloropentyl)benzene) was not detected, either. On the contrary, the new triplets, multiplets, and quintets at 0.89, 1.32, and 1.62 ppm assigned to Ph(CH₂)₄CH₃, Ph(CH₂)₂(CH₂)₂CH₃, and PhCH₂CH₂(CH₂)₂CH₃, respectively, were observed (Fig. 3b), as well as, the three new signals were coupled relationship in ¹H–¹H COSY NMR spectra (Fig. S6). At the same time, when the integral value of the peak at δ_H = 2.62 ppm (assigned to PhCH₂-) after subtracting the integral value of PhCH₂- in unreactive CPP was compared with the above respective integral values, the ratios were 2 : 2 : 4 : 3, indicating that a new compound, Ph(CH₂)₄CH₃ (pentylbenzene, PBZ), was generated. Accordingly, a detailed dechlorination mechanism of CPP under the hydrozirconation is illustrated in Scheme 3. Firstly, the TAI-Cl bearing a β-chlorine substituent was formed by the regioselective hydrozirconation of CPP with ZrH. Owing to the existence of the β-chlorine, Cp₂ZrCl₂ was eliminated and TAI-Cl was turned into a 5-phenyl-1-pentene. Subsequently, ZrH reacted selectively with the terminal C=C bond in 5-phenyl-1-pentene instead of the terminal C=C bond in CPP to form the TAI. Finally, the TAI was turned into Ph(CH₂)₄CH₃, after being quenched by acidified methanol.

It should be mentioned that Cp₂ZrCl₂ would be eliminated immediately when the hydrozirconation of CPP takes place. In addition, the

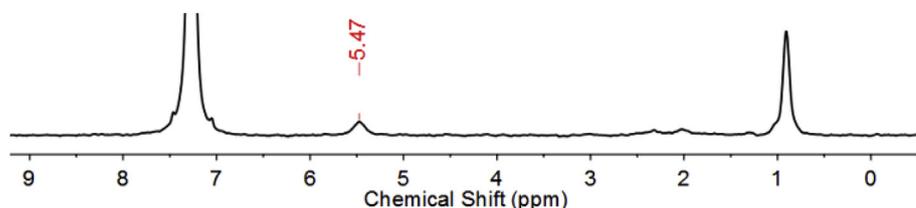


Fig. 2. ²H NMR spectrum (δCDCl₃ = 7.26 ppm) of PCP chain-scission products with D₂O quenched.

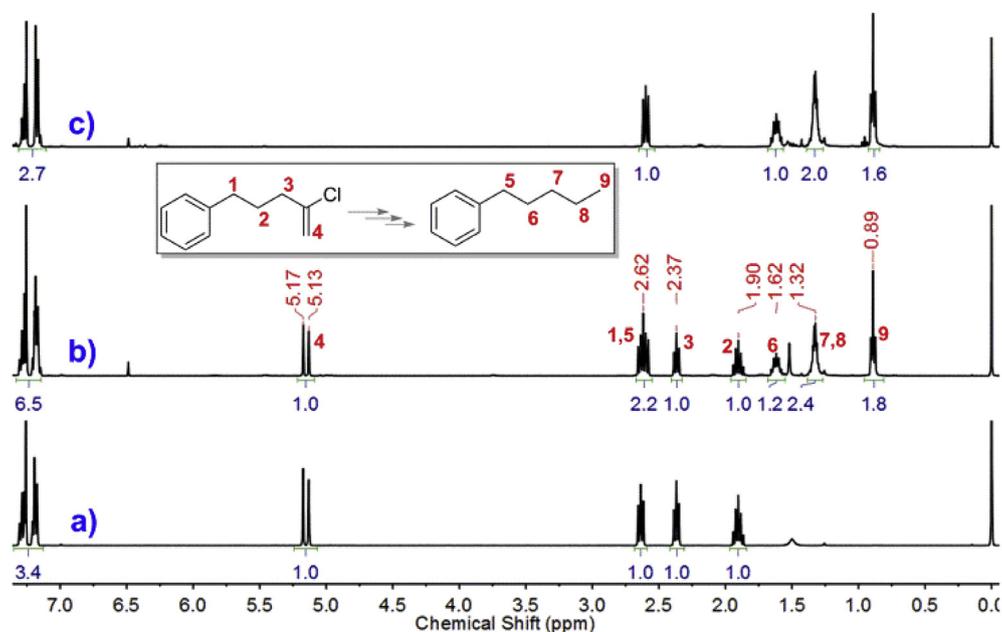
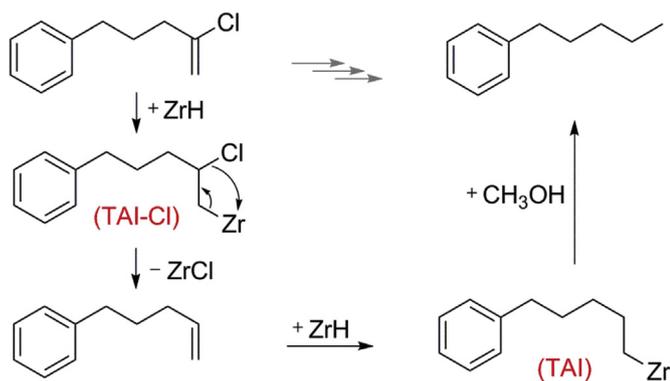


Fig. 3. ^1H NMR spectra of a) CPP; b-c) products after CPP hydrozirconation. Conditions: THF, 60 °C, 3 h, acidified methanol quenched, b) ZrH/CPP = 1.1; c) ZrH/CPP = 2.1.



Scheme 3. Dechlorination of CPP under the hydrozirconation. (Zr = Cp_2ZrCl).

Table 2

The conversion of CPP into PBZ after hydrozirconation of CPP under different molar ratio of [Zr] to [C=C].

Entry ^a	[Zr]/ [C=C] ^b	Integral value of characteristic structures ^c		PBZ: CPP ^d
		$\text{PhCH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$ (PBZ)	$\text{Ph}(\text{CH}_2)_3\text{CClCH}_2$ (CPP)	
1	0	0	1.0	0 : 1.0
2	1.1	1.2	1.0	1.2 : 1.0
3	2.1	1.0	0	1.0 : 0

^a Reaction conditions: THF, 60 °C, 3 h, acidified methanol quenched.

^b Molar ratio of ZrH and C=C bonds in CPP.

^c Calculated by NMR spectroscopy (Fig. 3).

^d Molar ratio of CPP and PBZ.

elimination of Cp_2ZrCl_2 and the subsequent hydrozirconation of the new generated C=C bonds from eliminating Cp_2ZrCl_2 were also simultaneously performed. The reasons were as follows: on one hand, (4-chloropentyl)benzene as the product generated from quenching hydrozirconation intermediate of CPP by methanol was not detected, suggesting that the elimination of Cp_2ZrCl_2 immediately occurred during the hydrozirconation of CPP. On the other hand, 5-phenyl-1-

pentene, as β -chlorine eliminated product of hydrozirconation intermediate of CPP, was not detected, either, indicating that 5-phenyl-1-pentene as intermediate was also immediately involved in the subsequent hydrozirconation while eliminating Cp_2ZrCl_2 . Furthermore, when 1.1 M ratio of ZrH to CPP was used to react (Fig. 3b), the molar ratio of pentylbenzene against the unreactive CPP was precisely 1.2 : 1.0 (entry 2 in Table 2), implying that just 0.55 mol CPP proceeded hydrozirconation with 0.55 mol ZrH and remaining 0.55 mol ZrH completely selectively reacted with 5-phenyl-1-pentene intermediate instead of CPP, which further supported the above inference. Meanwhile, all CPP could be converted into pentylbenzene when using 2.1 M ratio of ZrH reagent to CPP (entry 3 in Table 2, Fig. 3c and Fig. S7).

Accordingly, it can be concluded that the dechlorination plays a key role in subsequent hydrozirconation of in-situ formed C=C bonds from dechlorination. The reason may be the fact that ZrH is actually oligomers ($[\text{Cp}_2\text{ZrHCl}]_n$) [16] so that ZrH is the multicenter clusters enabling to multi-coordinate simultaneously. Namely, when a center zirconium in the cluster coordinate with the chloride in PCP, and the chloride is eliminated in the form of Cp_2ZrCl_2 to generate new C=C bonds, another center zirconium in the cluster is more facilely to be coordinated with new generating C=C bonds owing to more close distance compared with another ZrH clusters. Although dechlorination is in the favor of chain cleavage, more ZrH is consumed. However, we found that the problem could be resolved via the synergistic effects of ZrH with LiH and H_2 , in which the Cp_2ZrCl_2 could be transformed into ZrH, meaning that ZrH would be *in situ* regenerated constantly.

3.4. Catalytic cleavage of PCP under the synergism of ZrH with LiH and H_2

As shown in Table 3, under the synergistic action of ZrH with LiH and H_2 , the efficiently catalyzed chain scission has been achieved. It can be seen that, in the case of 0.05 M ratio of ZrH to C=C bonds (entry 2 in Table 3), PCP with $109.9 \text{ kg mol}^{-1}$ is cleaved to 1.3 kg mol^{-1} in the aid of LiH and H_2 . Further decreasing the molar ratio of ZrH reagent to 0.003, the catalyzed chain scission is still efficient, in which the M_n of chain-scission products is 13.6 kg mol^{-1} (entry 6 in Table 3).

In order to clarify the synergistic effects of ZrH with LiH and H_2 , control experiments were carried out. Firstly, the molar ratio of ZrH to

Table 3
The molecular weight and PDI of catalytic chain-scission products from PCP.

Entry	[Zr]/[C=C]/[Li] ^a	H ₂ ^b (atm)	M _n ^c (kg mol ⁻¹)	PDI ^c
1 ^d	–	0	109.9	2.14
2 ^d	0.05/1/0.5	10	1.3	1.63
3 ^d	0.01/1/0.5	10	5.1	1.50
4 ^e	0.01/1/0.5	20	2.5	1.45
5 ^e	0.005/1/0.5	20	4.7	1.73
6 ^e	0.003/1/0.5	20	13.6	1.71
7 ^d	0.05/1/0	0	12.8	2.33
8 ^d	0.05/1/0.5	0	6.7	1.95
9 ^d	0.05/1/0	10	10.6	2.26

^a Molar ratio of C=C bonds in PCP, ZrH, and LiH.

^b The pressure of H₂.

^c From GPC versus polystyrene standards (Fig. S8).

^d Reaction temperature is 60 °C.

^e Reaction temperature is 80 °C.

C=C bonds is 0.05 in the absence of both LiH and H₂, in this case, the M_n of chain-scission products is 12.8 kg mol⁻¹ (entry 7 in Table 3). In the cases of ZrH with LiH or H₂ alone, under the same ZrH loading, chain-scission products with the M_n of 6.7 or 10.6 kg mol⁻¹ (entry 8 and 9 in Table 3) were obtained, respectively. An interesting phenomenon should be noted, that chain-scission efficiency of ZrH with LiH is higher than that of ZrH with H₂ (entry 8 and 9 in Table 3). This is because β-alkyl elimination might be hampered due to the lack of ZrH attacking the new regenerated C=C bonds from Cp₂ZrCl₂ elimination. In the case of ZrH with H₂, the chain-end C–Zr bond in the chain-scission products could *in situ* regenerate ZrH with the help of H₂; however, because ZrH is regenerated restrictedly at the chain end of chain-scission products, regenerated ZrH might prefer to attack the chain-end C=C bonds in chain-scission products. Once regenerated ZrH reacts with chain-end C=C bonds bearing Cl substitute, it will be immediately turned into Cp₂ZrCl₂ and become inactive permanently as Cp₂ZrCl₂ could not be reduced into ZrH by H₂. Compared to the case of ZrH alone (entry 7 in Table 3), M_n of chain-scission product in the case of ZrH with H₂ is slightly lower (entry 9 in Table 3), indicating that only few regenerated ZrH induces the occurrence of chain scission. Hence, ZrH with H₂ could not realize efficiently catalytic chain scission. In the case of ZrH with LiH, eliminated Cp₂ZrCl₂ is free and will be constantly turned into ZrH until all of ZrH is involved in chain scission and transferred into the chain-end C–Zr bond of chain-scission products, as

C–Zr bond could not *in situ* regenerate ZrH with the help of LiH. Therefore, ZrH with LiH could achieve somewhat catalytic chain scission but not be sustainable catalysis. Accordingly, only with the synergistic help of both LiH and H₂, ZrH could achieve cyclic catalysis chain scission of PCP. In the cases of ZrH with LiH and H₂, the M_n of chain-scission products is the lowest (1.3 kg mol⁻¹, entry 2 in Table 3), demonstrating that PCP is catalytically cleaved by ZrH with the synergism of LiH and H₂.

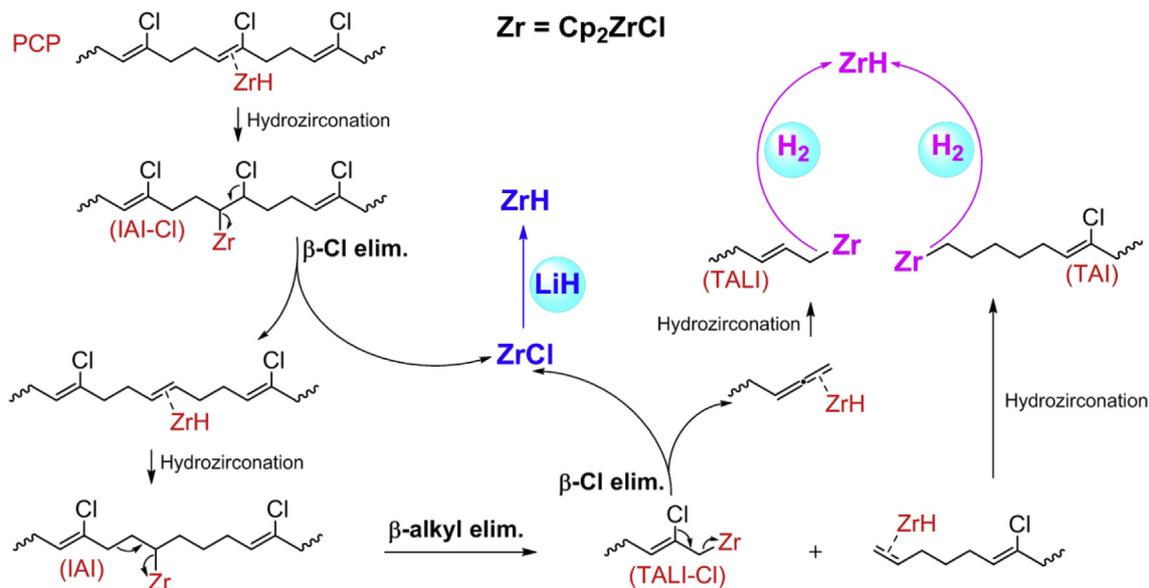
Scheme 4 shows possible catalytic cleavage pathway of PCP. Under the influence of ZrH, PCP will undergo a series of reactions, including hydrozirconation, β-Cl elimination and β-alkyl elimination, in which PCP is induced to perform β-Cl elimination to generate Cp₂ZrCl₂ and new C=C bonds, as long as β-Cl exists in alkylzirconium intermediates (such as IAI-Cl and TALI-Cl in Scheme 4). At the same time, alkylzirconium intermediates without β-Cl (IAI in Scheme 4) are induced to proceed β-alkyl elimination to achieve chain scission of PCP, and terminal alkylzirconium intermediates bearing chain-end C–Zr bond (such as TAI and TALI in Scheme 4) are formed. With the synergistic effects of both H₂ and LiH, chain-end C–Zr bonds in TAI and TALI and eliminated Cp₂ZrCl₂ will be constantly regenerated ZrH to realize cyclic catalytic chain scission of PCP.

4. Conclusions

PCP could be cleaved into oligomers by ZrH under mild conditions. The molecular weights of chain-scission products were well controlled by the feeding of ZrH. At the same time, no side reactions took place during chain scission, namely, the chain structures of PCP could be maintained into the chain-scission products. More importantly, the chlorine self-assisted β-alkyl elimination mechanism in PCP was clarified by both of PCP system and model compound CPP system. The elimination of Cp₂ZrCl₂ played a critical step not only to hydrozirconation of new generating C=C bonds from PCP dechlorination, but also to subsequent β-alkyl elimination of IAI. With the help of well-defined mechanism, catalytic cleavage of PCP was realized via regenerating *in situ* ZrH reagent under the synergistic effect of ZrH with LiH and H₂.

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Scheme 4. Catalytic cleavage pathways of PCP in the presence of ZrH with LiH and H₂.

the key project (no. 51233005).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2019.03.007>.

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