

Supporting information for

Stepwise synthesis of Zr-C-Si main chain polymer precursor for ZrC/SiC/C composite ceramics

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Supporting information 1

In order to prove the reactivity of $\text{Cp}_2\text{Zr(II)}$ and $\cdot\text{MgCl}$ active specie, the PZCS-1 was characterized by using FTIR spectroscopy. As shown in **Figure S1a**, the main peaks of $1411/1264\text{ cm}^{-1}$ was ascribed to Si-CH₃ bending vibrations, the $814/1445\text{ cm}^{-1}$ peak could be attributed to C-H bending vibrations in Cp, and the weaker peak at 2927 cm^{-1} corresponded to -CH₂- structure. It is worth noting that the C-H stretching vibration peak of the terminal olefin -CH=CH₂ at 3070 cm^{-1} disappeared by comparing the FTIR spectra of PZCS-1 with $\text{CH}_3\text{Si}(\text{CH}=\text{CH}_2)\text{Cl}_2$, indicating that a reaction occurred at the terminal olefin. This result was also confirmed by the ¹HNMR results in **Figure S1b**. The chemical shift value of 6.18~6.27 ppm was ascribed to the characteristic peak of internal C-H of -CH=CH₂, and the 6.05~6.15 ppm peaks corresponded to the terminal C-H of -CH=CH₂. Of note, the two C-H peaks in -CH=CH₂ were absent by comparing the spectra of PZCS-1 with $\text{CH}_3\text{Si}(\text{CH}=\text{CH}_2)\text{Cl}_2$, indicating that the vinyl bond was broke under the impact of $\text{Cp}_2\text{Zr(II)}$. Meanwhile, the Mn and Mw of PZCS-1 were measured to be 1013 and 1833 g/mol respectively, through GPC analysis, indicating the polymerization of vinyl group to

construct a saturated main chain of single bonds. From the above-mentioned structural characterization of PZCS-1, we concluded that the reaction of Cp_2ZrCl_2 with Mg indeed generated soluble active species being able to trigger the polymerization of vinyl group. It was thus worthy to deeply analyze the polymerization mechanism, namely the role of $\text{Cp}_2\text{Zr(II)}$ and $\cdot\text{MgCl}$ active species in constructing a polymeric chain. Since zirconocene compounds are commonly used as olefin polymerization catalysts^[19-21] and we believed the mechanism of coordination insertion polymerizations of 1-olefin by metallocenes^[13, 14] would inspire our understanding on the role of $\text{Cp}_2\text{Zr(II)}$ in creating a polymeric structure in PZCS-1. In the first step (step 1 in **Figure S1c**), the two Zr-Cl bonds in Cp_2ZrCl_2 (1) were broken by Mg to form free radicals of $\text{Cp}_2\text{Zr(II)}$ (2) and $\cdot\text{MgCl}$ (3). In the subsequent reaction (step 2), $\text{R}\cdot$ radicals were generated through the atom transfer between $\cdot\text{MgCl}/\text{Cp}_2\text{Zr(II)}$ and R-Cl . In the third step (step 3), one of the free electrons in $\text{Cp}_2\text{Zr(II)}$ (2) combined with $\text{R}\cdot$ radical to generate a zirconocene catalyst (5) with single active site. And last, the silene monomer was inserted into the active center of zirconocene catalyst and brought the regeneration of the active center (6) to continue the polymerization of olefin (7). During the whole polymerization process, these organometals would not split off from the reacting site but rather stay there for chain propagation like an initiator, which provides the possibility of synthesizing metal-containing polymers. However, the content of Zr in our prepared PZCS-1 was limited because Zr only existed at the end-capping but not in the main chain.

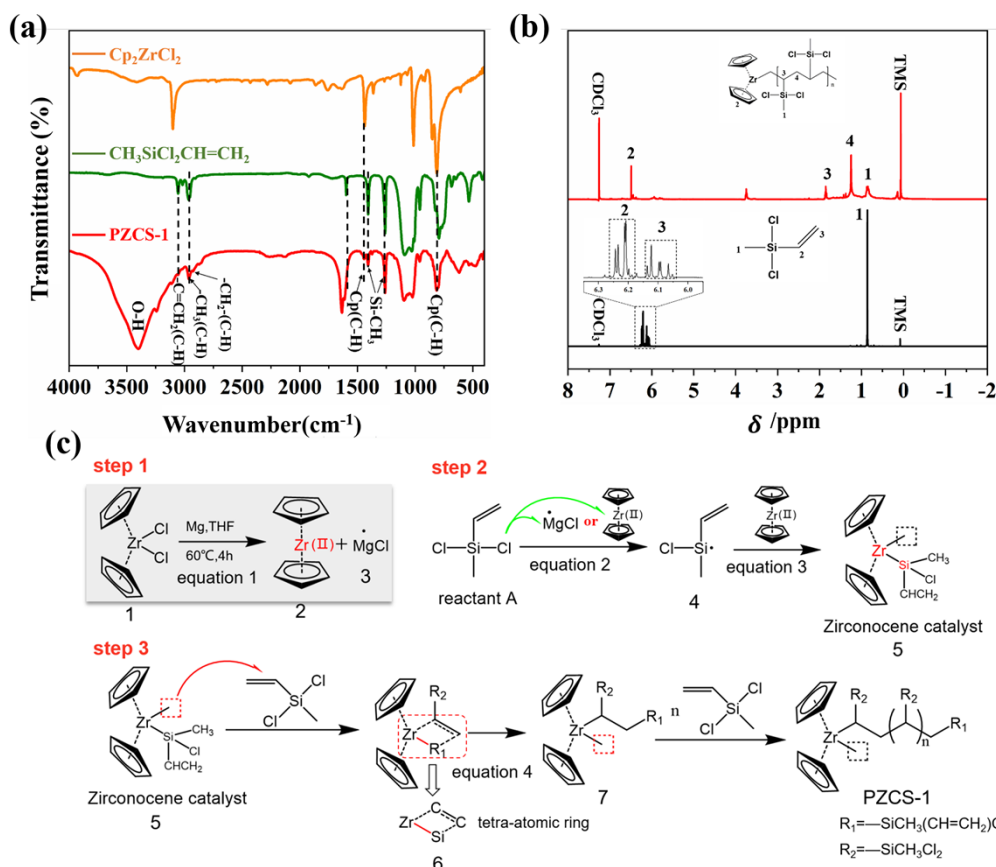


Figure. S1 (a) FTIR spectra of PZCS-1, Cp₂ZrCl₂ and CH₃Si(CH=CH₂)Cl₂, (b) ¹H-NMR spectra of PZCS-1 and CH₃Si(CH=CH₂)Cl₂ and (c) the proposed reaction pathway of PZCS-1.

Supporting information 2

In order to further explain the polymerization reaction mechanism of Cp₂Zr(II)/·MgCl/THF system and SiCH₃(CH=CH₂)Cl₂, for comparison, a chemical monomers that do not contain Si-Cl bonds was selected. When Si(CH₃)₃(CH=CH₂) was used as the reactant instead of SiCH₃(CH=CH₂)Cl₂, the obtained sample only possessed a Mn of 324 g/mol a Mw of 373 g/mol analyzed from GPC result, which meant no polymerization occurred, and the possible reactions are shown in Figure S2 through previous research work.

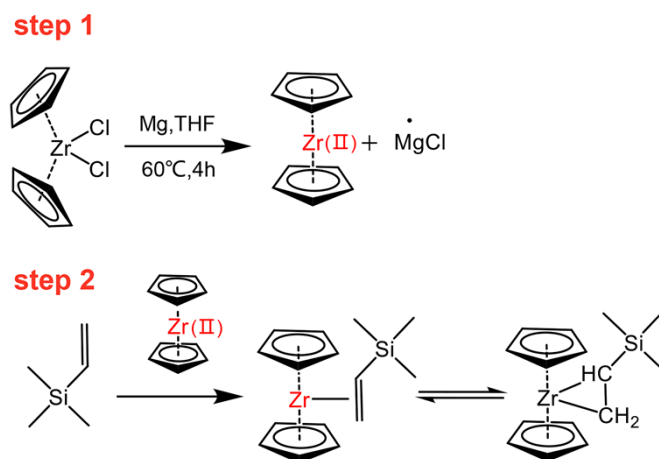


Figure. S2 The reaction process of $(\text{CH}_3)_3\text{Si}(\text{CH}=\text{CH}_2)$ and Cp_2Zr :

Supporting information 3

The ideal reaction pathway for the synthesis of PZCS-2 precursor containing Zr-C-Si backbone structure by the reaction of $\text{Cp}_2\text{Zr}(\text{II})/\cdot\text{MgCl}$ with $(\text{CH}_3)_2\text{Si}(\text{CH}_2\text{Cl})_2$. The ideal pathway mainly includes three steps of (i) $\text{Cp}_2\text{Zr}(\text{II})$ attracted Cl atoms to generated R: radicals and Cp_2ZrCl_2 ; (ii) R: radical and $\cdot\text{MgCl}$ reversibly generated Grignard reagent of ClMg-R-MgCl at high temperature, and (iii) the Grignard reaction occurred between ClMg-R-MgCl and Cp_2ZrCl_2 , as shown in Figure S3.

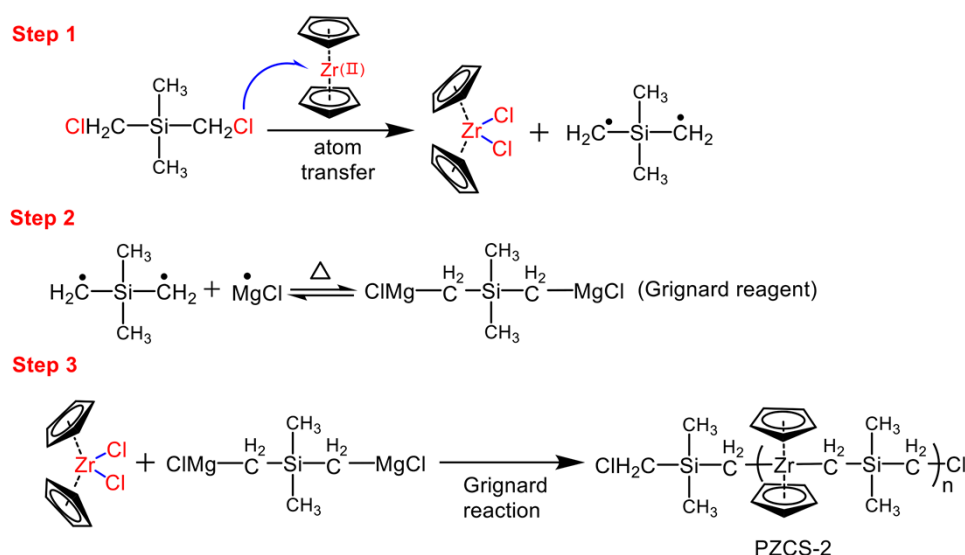


Figure. S3 The ideal reaction pathway for the synthesis of PZCS-2 precursor

Supporting information 4

The pyrolysis process of the PZCS-2 precursor was studied using 3D-FTIR -GC-MS diagrams of the volatile products. The gaseous products released by PHCS at 270 and 800 °C were injected in the GC-MS system. At 180 °C, the solvents toluene ($m/z=92$), tetrahydrofuran ($m/z=72$) and part of the water was evaporated, of note, the small $\text{Si}^{3+}\text{-CH}_3$ molecules ($m/z=43$) appeared in the low temperature section, corresponding to 1256 cm^{-1} in the 3D-FTIR spectrum (Figure S4-1), indicating that some Si-containing fragments are broken and volatilized. At the same time, CO_2 ($m/z=44$) was detected by GC-MS. According to 3D-FTIR analysis, when the temperature is above 240 °C, the Hf-Cp bond breaks to generate volatile cyclopentadiene (Cp) ($m/z=66$), which mainly corresponds to the C-H vibration of Cp at 868 cm^{-1} . With the temperature rises, the Cp undergoes thermal cracking and rearrangement, as shown in Figure S3, the $\text{C}\equiv\text{C}$ - peak at 2290 cm^{-1} , the C-H peak at 2930 cm^{-1} corresponding to $-\text{CH}_2-$, and the C-H at 2968 cm^{-1} corresponding $-\text{CH}_3$ was found in 3D-FTIR, which suggests that Cp cracks to generate small molecules such as propane ($m/z=44$) and propyne ($m/z=40$)(Figure S4-2).

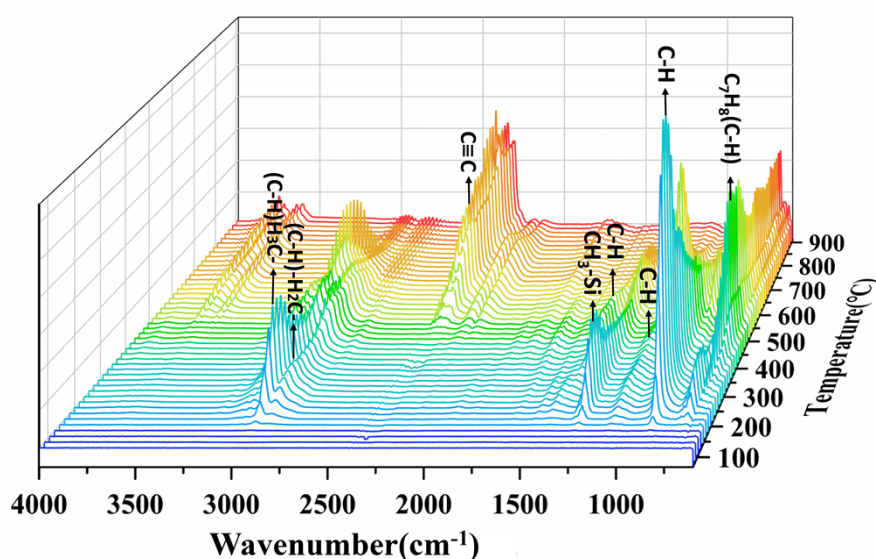


Figure. S4-1 3D-FTIR spectra of the gaseous products of PZCS precursor pyrolyzed at different temperatures

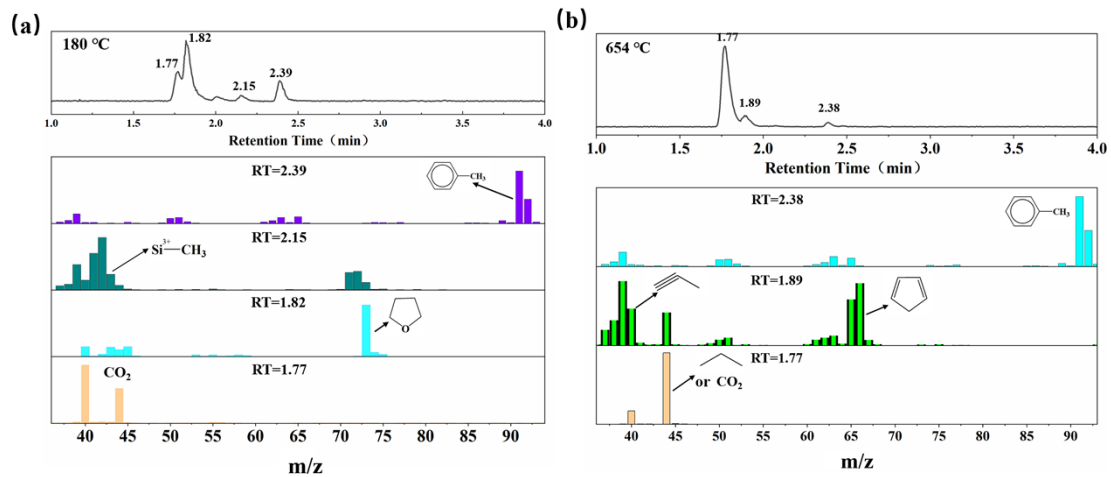


Figure. S4-2 GC-MS chromatograms of the evolved gases decomposition from PZCS precursor at 180 °C (a) and 654 °C (b)

Supporting information 5

The XPS survey spectra in Figure S5 indicate the presence of Zr, C, Si and O elements. Although PZCS is a kind of oxygen-free precursor in theory, the transfer and preservation may introduce some unexpected O element, and thus it is found in the XPS survey spectra.

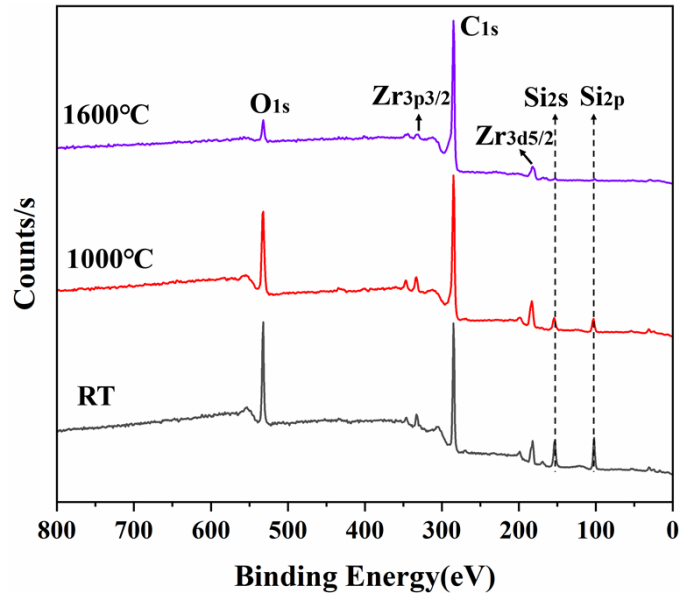


Figure. S5 XPS survey spectra of PZCS precursor at different temperature