Fourier-transform infrared spectroscopy (FT-IR) analysis was also performed. The samples were pressed into KBr pellets and analyzed using a Thermo Nicolet Avatar 360 FT-IR spectrometer, with a scan range of 400-4000 cm\(^{-1}\) and resolution of 4 cm\(^{-1}\). A Bruker AV 400 nuclear magnetic resonance (NMR) spectrometer was used to perform \(^1\)H-NMR and \(^{29}\)Si-NMR measurements, with deuterated chloroform (CDCl\(_3\)) as the NMR solvent.

Fig. S1 FT-IR spectra of M\(_L\), M\(_M\) and M\(_H\)

The FT-IR analysis of M\(_L\), M\(_M\) and M\(_H\) is shown in Figure S1. The most important characteristic peaks in the FT-IR spectra are as follows: C-H vibration peaks at 2950 and 2900 cm\(^{-1}\), Si-H vibration peaks at 2100 cm\(^{-1}\), C-H in Si-CH\(_3\) deformation vibrations peaks at 1400 cm\(^{-1}\), CH\(_2\) in Si-CH\(_2\)-Si out-of-plane rocking vibrations peaks at 1350 cm\(^{-1}\), CH\(_3\) in Si-CH\(_3\) deformation vibrations peaks at 1250 cm\(^{-1}\), Si-C-Si in Si-CH\(_2\)-Si stretching vibrations peaks at 1020 cm\(^{-1}\) and Si-C stretching vibrations at 820 cm\(^{-1}\). The three samples all contain the same peaks, indicating that the functional groups are basically the same. The intensity ratio between the characteristic absorption peaks of Si-H and Si-CH\(_3\) in the FT-IR spectra, I\(_{Si-H}/I_{Si-CH_3}\), was used to characterize the Si-H content of PCS. The results are shown in Table S1. From M\(_L\) to M\(_H\), the content of Si-H bond in samples decreases gradually, which indicates that the degree of polycondensation of M\(_L\), M\(_M\) and M\(_H\) increases gradually.
Table S1 Parameters of structural units of $M_L$, $M_M$ and $M_H$

| Samples | FT-IR | $^1$H-NMR | $^{29}$Si-NMR |
|---------|-------|-----------|--------------|
|         | $I_{\text{Si-H}}/I_{\text{Si-CH}_3}$ | $A_{\text{Si-H}}/A_{\text{C-H}}$ | $A_{\text{SiC}_3\text{H}}/A_{\text{SiC}_4}$ |
| $M_L$   | 0.93  | 0.21      | 0.51         |
| $M_M$   | 0.89  | 0.18      | 0.45         |
| $M_H$   | 0.82  | 0.14      | 0.40         |

Fig. S2 The $^{29}$Si-NMR spectra of $M_L$, $M_M$ and $M_H$

The $^{29}$Si-NMR analysis of $M_L$, $M_M$ and $M_H$ is shown in Figure S2. In the $^{29}$Si-NMR spectra, the two characteristic peaks around $\delta = -17.2$ and $\delta = 0$ are the resonance peaks of Si atoms in SiC$_3$H and SiC$_4$ structures respectively. The ratio of the two structures can be obtained by calculating the ratio between their corresponding characteristic peak areas, and the results are also listed in Table S1. The peak intensity of SiC$_3$H structure decreases significantly too. Although the structure of PCS is complex, it can be considered as be composed of the following two structural units. The moles of the two structures can be calculated based on Mn and $A_{\text{SiC}_3\text{H}}/A_{\text{SiC}_4}$. The results are shown in Table S2.

$$\text{SiC}_3\text{H} \quad \text{SiC}_4$$

The $^{29}$Si-NMR analysis of $M_L$, $M_M$ and $M_H$ is shown in Figure S3. In the $^1$H-NMR spectra, the two characteristic peaks around $\delta = 4.0-5.0$ and $\delta = 0$ correspond to the characteristic peaks of H in Si-H and C-H respectively. The ratio of the two
structures are also listed in Table S1. C-H peaks in $^1$H-NMR spectra can be further subdivided into C-H peaks in Si-CH$_3$, C-H peaks in Si$_2$CH$_2$ and C-H peaks in Si$_3$CH. Si$_2$CH$_2$ content can be used to characterize the content of linear structures in the molecule. Si$_3$CH content can be used to characterize the content of branched and cyclic structures in the molecule. It can be seen that from M$_L$ to M$_H$, the degree of condensation of molecules increases gradually, and the content of branched and cyclized structures increases. Si-H peak can be subdivided into Si-H on the condensed ring (CR) structure, single ring (SR) structure and linear (L) structure [1]. The ratio of the three structures can be obtained by calculating the ratio among their corresponding characteristic peak areas. According to the moles of SiC$_3$H and SiC$_4$, and the ratio of Si-H on different structures, the moles of each Si-H can be obtained. And the results are listed in Table S2.

| Samples | SiC$_3$H /mol | SiC$_4$ /mol | Si-H$_{(L)}$ /% | Si-H$_{(SR)}$ /% | Si-H$_{(CR)}$ /% | Si-H$_{(L)}$ /mol | Si-H$_{(SR)}$ /mol | Si-H$_{(CR)}$ /mol |
|---------|---------------|--------------|----------------|----------------|----------------|----------------|----------------|----------------|
| M$_L$   | 1.9           | 3.8          | 28.0           | 27.3           | 44.6           | 0.51           | 0.54           | 0.85           |
| M$_M$   | 4.6           | 10.2         | 25.2           | 26.9           | 47.9           | 1.2            | 1.2            | 2.2            |
| M$_H$   | 8.7           | 21.8         | 24.7           | 24.7           | 50.5           | 2.2            | 2.2            | 4.4            |

All the data in the table are calculated according to the peak area ratio of $^{29}$Si-NMR and $^1$H-NMR, and the trend of variation is consistent with the previous analysis. According to the moles of each structure in the table, M$_L$, M$_M$ and M$_H$ should have the
following molecular model:

\[ M_L \]

\[ M_M \]

\[ M_H \]

Fig. S4 Molecular model of \( M_L \), \( M_M \) and \( M_H \)

It can be seen from the molecular model that \( M_L \), \( M_M \) and \( M_H \) are PCS with the same Si-C main chain and different degrees of condensation. With the condensation reaction carried out, the branching and ring structure of molecules increase, and the length of molecular chains increases. The two changes above have different effect on the linearity of molecules.
Fig. S4 Digital pictures of PCS fibers of different diameters

| Samples   | Melt point (°C) | Spinning temperature (°C) | Spinning pressure (MPa) | Winding speed (m · min⁻¹) |
|-----------|----------------|----------------------------|-------------------------|---------------------------|
| LPCS      | < 20           | --                        | --                      | --                        |
| PCS-2     | 104-124        | 195                       | 0.25                    | 290                       |
| PCS-6     | 158-175        | 253                       | 0.2                     | 235                       |
| PCS-8     | 180-200        | 304                       | 0.25                    | 290                       |
| PCS-10    | 214-244        | 337                       | 0.2                     | 235                       |
| PCS-10-2  | 245-279        | 381                       | 0.3                     | 235                       |
| PCS-16    | 256-287        | 400                       | 0.5                     | 180                       |
| PCS-24    | > 300          | ---                       | ---                     | ---                       |

Reference
[1] Bagnall K W. Advances in inorganic chemistry and radiochemistry[J]. Journal of
