Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary materials

Transparent cyclo-linear polyphenylsiloxane elastomer integrating high refractive index, thermal stability and flexibility

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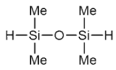
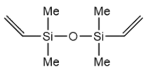
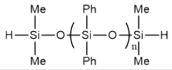
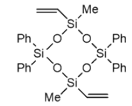
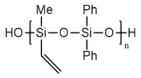
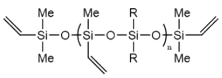
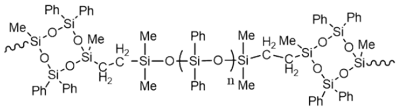
Table S1 Abbreviation of molecular name and corresponding molecular structure.

Abbreviation	**DPSD**	molecular structure	
		Chemical name	diphenylsilanediol
	HMM	molecular structure	
		Chemical name	1,1,3,3-tetramethyldisiloxane
	DMVS	molecular structure	
		Chemical name	dichloromethylvinylsilane
	ViMM	molecular structure	
		Chemical name	1,3-divinyl-1,1,3,3-tetramethyldisiloxane
	PDPh	molecular structure	
		Chemical name	polydiphenylsiloxane oligomer
	H-Ph-Linear	molecular structure	
		Chemical name	α,ω-bis(dimethylsiloxyl)polydiphenylsiloxane oligomer
	ViPh-Cyclo	molecular structure	
		Chemical name	1,5-dimethyl-1,5-divinyl-3,3,7,7-tetraphenylcyclotetrasiloxane
	ViPh-Crosslinker	molecular structure	
		Chemical name	α,ω-bis(hydroxyl)poly(methylvinylsiloxane-diphenylsiloxane)
	Vi-ViPh-Crosslinker	molecular structure	
		Chemical name	α,ω-bis(dimethylvinylsiloxyl)poly(methylvinylsiloxane-diphenylsiloxane) oligomer
	Ph-CLS	molecular structure	
		Chemical name	cyclo-linearly structured phenyl polysiloxane

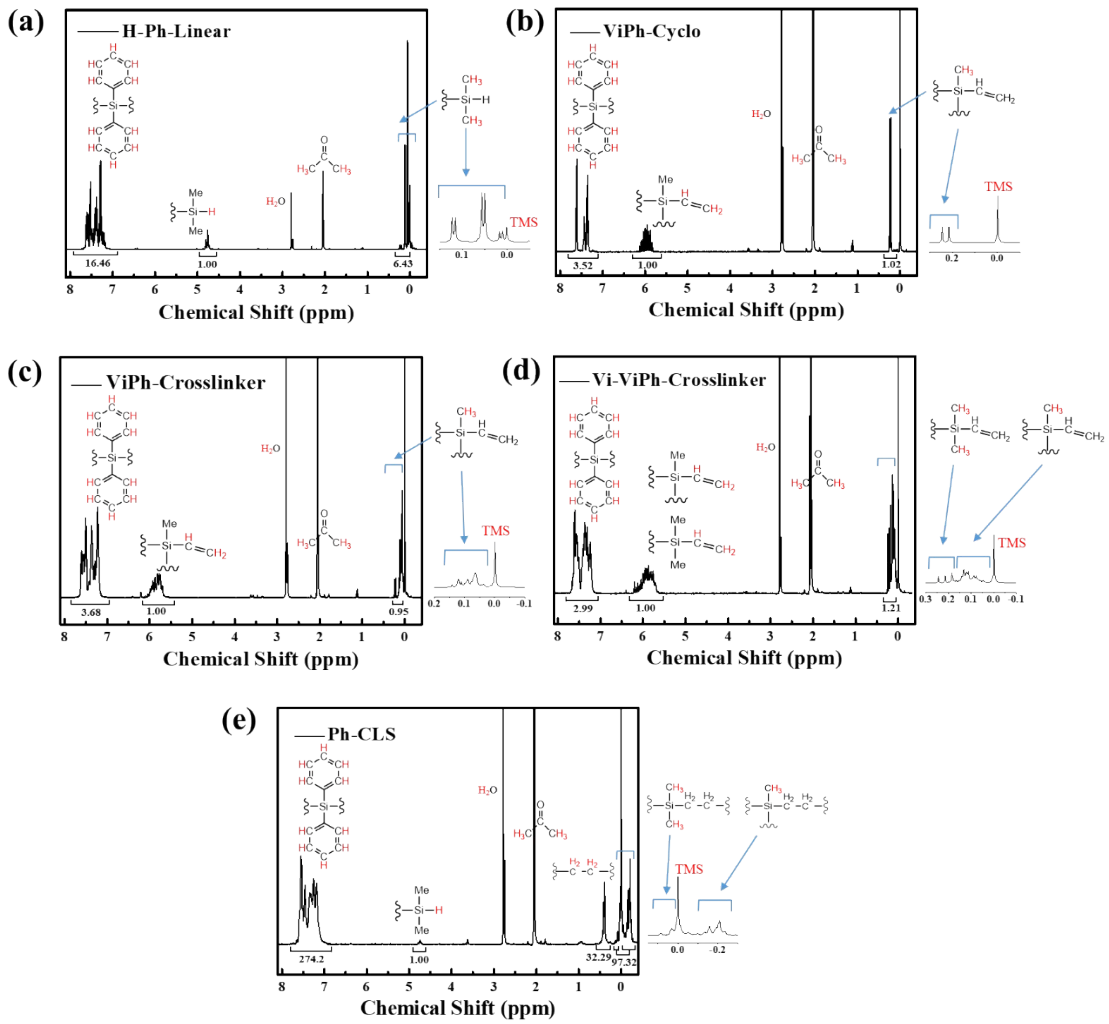


Fig. S1 The ^{1}H-NMR spectra of (a) H-Ph-Linear, (b) ViPh-Cyclo, (c) ViPh-Crosslinker, (d) Vi-ViPh-Crosslinker and (e) Ph-CLS.

Table S2 The molar ratio of different type of H in the ^{1}H-NMR spectra of H-Ph-Linear, ViPh-Cyclo, ViPh-Crosslinker, Vi-ViPh-Crosslinker and Ph-CLS.

assignment / sample	Hydrogen atom ratio[α]				
	-$C_6\underline{H}_5$	-C$\underline{H}$=C$\underline{H}_2$	-Si-$\underline{H}$	-C$\underline{H}_2$-C$\underline{H}_2$-	-C$\underline{H}_3$
	7.1~7.7 ppm	5.8~6.15 ppm	4.7~4.85 ppm	0.3~0.5 ppm	-0.25~0.3 ppm
H-Ph-Linear	16.46	/	1.00	/	6.43
ViPh-Cyclo	3.52	1.00	/	/	1.02
ViPh-Crosslinker	3.68	1.00	/	/	0.95
Vi-ViPh-Crosslinker	2.99	1.00	/	/	1.21
Ph-CLS	274.2	/	1.00	32.29	97.32

[α] The peaks of acetone (2.05 ppm), TMS (0.0 ppm) and water (2.84 ppm) in the spectra come from the commercial deuterated acetone solvent.

Table S3 The molar ratio of different groups in H-Ph-Linear, ViPh-Cyclo, ViPh-Crosslinker, Vi-ViPh-Crosslinker and Ph-CLS according to ^{29}Si-NMR and ^{1}H-NMR spectra.

assignment / sample	Group ratio					
	methods	**-Ph**	**-Si-H**	**-CH_3**	**-CH=CH_2**	**-CH_2-CH_2-**
H-Ph-Linear	^{1}H-NMR	3.29	1.00	2.14		
	^{29}Si-NMR	2.97	1.00	2.00		
	Theoretical (n=3)	3.00	1.00	2.00		
ViPh-Cyclo	^{1}H-NMR	2.11		1.02	1.00	
	^{29}Si-NMR	2.02		1.00	1.00	
	Theoretical	2.00		1.00	1.00	
ViPh-Crosslinker	^{1}H-NMR	2.21		0.95	1.00	
	^{29}Si-NMR	2.22		1.00	1.00	
	Theoretical (n=11)	2.00		1.00	1.00	
Vi-ViPh-Crosslinker	^{1}H-NMR	1.79		1.21	1.00	
	^{29}Si-NMR	1.62		1.25	1.00	
	Theoretical (n=5, 75% end-capping)	1.54		1.23	1.00	
Ph-CLS	^{1}H-NMR	6.03	0.11	3.66		1.00
	^{29}Si-NMR	5.92	0.14	3.31		1.00
	Theoretical (L:C=1.17:1)$^{\beta}$	5.51	0.17	3.34		1.00

$^{\beta}$ "L" and "C" represents H-Ph-Linear ("L") and ViPh-cyclo ("C") respectively. The molar ratio of Si-H: Si-Vi in the starting materials is 1.2:1. The end groups of Ph-CLS molecular chain should be Si-Hs.

Preparation and characterization of PDPh and H-Ph-Linear:

The synthesis of PDPh and H-Ph-Linear is shown in Scheme 1(a). It is worthy mention that in the synthesis of PDPh, DPSD was self-condensed without using any catalyst and solvent. The self-condensation reaction of DPSD and the end-capping reaction of PDPh with HMM were well carried out which were monitored by **FT-IR (Fig. 1(a))**, **^{1}H-NMR spectra (Fig. S1 (a), Table S2 and Table S3), ^{29}Si-NMR spectra (Fig. 1(c))** and **MALDI-TOF spectra (Fig. S2 (a) and S2 (b))**.

In the **FT-IR spectra (Fig. 1(a))** of PDPh, the strong absorptions around 1020–1140 cm^{-1} are assigned to the anti-symmetric stretching of Si–O bond, and the peaks at 1593 cm^{-1} and 1429 cm^{-1} are assigned to the phenyl C=C stretching and Si-phenyl stretching. After the end-capping reaction, the absorptions at 3315 cm^{-1} and 3626 cm^{-1} attributed to Si-O-H stretching in PDPh almost disappeared. Instead, new peaks at 2129 cm^{-1} and 1253 cm^{-1} assigned to Si-H and Si–CH_3

respectively, which appear in the spectrum of H-Ph-Linear which demonstrated that the end-capping reaction has been nearly completed.

In the **^{1}H-NMR spectra (Fig. S1 (a)),** the peaks at 7.1~7.7ppm, 4.7~4.85ppm and 0.0~0.15ppm can be assigned to H atoms in –Si-$C_6\underline{H}_5$, - Si-$\underline{H}$ and - Si-$C\underline{H}_3$ groups of H-Ph-Linear, respectively (The integral peak area ratio is shown in **Table S2**), which is consistent with the FT-IR results. There are no other peaks except for these peaks and the peaks of acetone (2.05 ppm), TMS (0.0 ppm) and water (2.84 ppm) come from the commercial deuterated acetone solvent, indicating that the product is very pure.

In the **^{29}Si-NMR spectra (Fig. 1(c))**, the M and D^m represents Si atoms in $R_3\underline{Si}$-O and $R_2\underline{Si}O_2$- respectively, and the m represents the number of condensed oxygen attached to a Si atom (Si-$\underline{O}$-Si). The peak of D^0 (-33.2 ppm) which assigned to Si in monomer DPSD disappears in PDPh, while the peaks of D^1 (corresponds to half condensed Si of -$Ph_2\underline{Si}$-OH) and D^2 (corresponds to fully condensed Si of -$Ph_2\underline{Si}$-O-) appeared. When the reaction temperature is controlled at 140℃ or below, the product is considered linear with no cyclic peaks (D_3Ph at -33.7ppm, D_4Ph at -42.8ppm) can be observed in ^{29}Si-NMR spectrum. The degree of condensation (DOC) of the PDPh can be calculated by the peak area ratio of each kind of Si (presents in Table 1) according to eqn (S1-1). It shows that the DOC of PDPh is 66% and the average molecular weight calculated according to eqn (S1-2) is 583 corresponding to n= ~3.

DOC (%) of PDPh =

$$\frac{D^1 + 2D^2}{2\left(D^0 + D^1 + D^2\right)} \times 100 \qquad (S1-1)$$

Molecular weight of PDPh =

$$\frac{2(D^1 + D^2) \cdot M_{DPSD}}{D^1} \qquad (S1-2)$$

In addition, M_{DPSD} (-Ph_2Si-O-) = 198.3g/mol.

After the end-capping reaction, the D^1 (-39.6 ppm) peak representing -$Ph_2\underline{Si}$-OH in H-Ph-Linear, nearly disappeared, and the M^H peak (-4.1 ppm) assigned to Si of -$Me_2\underline{Si}$-H present. The DOC and degree of end-capping of H-Ph-Linear can be calculated according to eqn (S2-1) and (S2-2) respectively (presents in Table 1), and the molar ratio of each type of Si can be obtained from the corresponding peak area ratio of ^{29}Si NMR. The calculated end-capping ratio of H-Ph-Linear is ca. 98.6% and the average molecular weight calculated according to eqn (S2-3) is 715.

DOC (%) of H-Ph-Linear =

$$\frac{D^1 + 2D^2 + M^H}{2(D^0 + D^1 + D^2) + M^H} \times 100 \qquad (S2-1)$$

End-capping ratio (%) of H-Ph-Linear =

$$\frac{M^H}{D^1 + M^H} \times 100 \qquad (S2-2)$$

Molecular weight of H-Ph-Linear =

$$\frac{2\left[M^H \cdot M_{HMM} + (D^1 + D^2) \cdot M_{DPSD}\right]}{M^H + D^1} \qquad (S2-3)$$

M_{HMM} (-$O_{1/2}$-Me_2Si-H) = 67.1 g/mol, M_{DPSD} (-Ph_2Si-O-) = 198.3g/mol.

The **MALDI-TOF result (Fig. S2(a))** of PDPh shows that the m/z peaks 634.9 and 833.3 perfectly match the proposed molecular formula combined with Na^+ for n of 3 and 4 respectively, and the **MALDI-TOF result (Fig. S2(b))** of H-Ph-Linear shows that the m/z peaks 552.8, 750.2 and 949.1 match the proposed molecular formula after end-capping combined with Na^+ for n of 2, 3 and 4 respectively. Moreover, the main peak in the spectrum is at n = 3, which generally agrees with the results from FT-IR and ^{29}Si-NMR.

Preparation and characterization of ViPh-Cyclo, ViPh-Crosslinker and Vi-ViPh-Crosslinker:

ViPh-Cyclo and ViPh-Crosslinker were prepared as described in scheme 1(b) and 1(c). The molecular structure of ViPh-Cyclo was confirmed by **FT-IR (Fig. 1(b))**, **^{1}H-NMR spectra (Fig. S1 (b-d), Table S2 and Table S3), ^{29}Si-NMR (Fig. 1(d))** and **MALDI-TOF (Fig. S2 (c-e), Table S4 and Table S5)**.

Characterization of ViPh-Cyclo:

In the **FT-IR spectra (Fig. 1(b))** of ViPh-Cyclo, the strong absorption around 1020–1140 cm^{-1} are assigned to the anti-symmetric stretching of Si–O bond, and the peaks at 1593 cm^{-1} and 1429 cm^{-1} is assigned to the phenyl C=C stretching and Si-phenyl stretching respectively. In addition, peaks at 961 cm^{-1} and 1256 cm^{-1} assigned to vinyl group and Si–CH_3 respectively appear in the spectrum. There is no -OH peak in the range of 3100-3800 cm^{-1} because of its cyclic structure.

In the **^{1}H-NMR spectra (Fig. S1 (b)** and **Table S2),** the peaks at 7.1~7.7ppm, 5.8~6.15ppm and 0.2~0.25ppm can be assigned to H atoms in –Si-$C_6\underline{H}_5$, - Si-C$\underline{H}$=C$\underline{H_2}$ and - Si-C$\underline{H_3}$ groups of ViPh-Cyclo, respectively. The molar ratio of “-Ph”： “-CH_3”： “-CH=CH_2” groups is 2.11：

1.02：1.00 (The integral peak area ratio is shown in **Table S3**)，which is consistent with the expected structure (scheme 1(b)).

In the **^{29}Si-NMR spectra (Fig. 1(d))** of ViPh-Cyclo, only the peaks of D^2 (-44.8ppm, assigned to Si of -Ph_2Si-O-) and $D^{2'}$ (-30.6 ppm, assigned to Si of -MeViSi-O-) appear. And the molar ratio of -Ph_2Si-O-:-MeViSi-O- is 0.99:1 (Table 1), which is completely consistent with our expected structure (scheme 1(b)).

The molecular structure was further verified by **MALDI-TOF (Fig. S2(c))**, the results show that the m/z peak 591 perfectly matches the proposed molecular formula combined with Na^+ (568+23) for ViPh-Cyclo.

Characterization of ViPh-Crosslinker:

In the **FT-IR spectra (Fig. 1(b))** of ViPh-Crosslinker, the strong absorption around 1020–1140 cm^{-1} is assigned to the anti-symmetric stretching of Si–O bond, and the peaks at 961 cm^{-1} and 1256 cm^{-1} are assigned to vinyl group and Si–CH_3. There is only a small amount of silanol (peak at 3620 cm^{-1}, Si-OH in -Ph_2Si-OH and -MeViSi-OH) remained after the reaction, indicating that the condensation reaction is nearly completed.

In the **^{1}H-NMR spectra (Fig. S1 (c)** and **Table S2),** the peaks at 7.1~7.7ppm, 5.8~6.15ppm and 0.0~0.2ppm can be assigned to H atoms in –Si-C_6H_5, - Si-CH=CH_2 and - Si-CH_3 groups of ViPh-Crosslinker, respectively. The molar ratio of "-Ph"：“-CH_3”：“-CH=CH_2”groups is 2.21：0.95：1.00 (The integral peak area ratio is shown in **Table S3**)，which is consistent with the expected structure (scheme 1(b)).

In the **^{29}Si-NMR result (Fig. 1(d))** of ViPh-Crosslinker, the large amount of $D^{2'}$ (-33.1 to -34.2 ppm, assigned to Si of -MeViSi-O-) and D^2 (-46.5 to -47.7 ppm, assigned to Si of -Ph_2Si-O-) were clearly detected, which verified the fully condensation of Si-O-Si. Moreover, the relatively low amount of $D^{1'}$ (-27.4 to -27.8 ppm, assigned to Si of -MeViSi-OH) and D^1 (-39.8 to -40.2 ppm, assigns to Si of -Ph_2Si-OH) were also found. The DOC and the molecular weight of ViPh-Crosslinker can be calculated according to eqn (S3-1) and (S3-2), and the results are listed in Table 1, which shows the DOC of the ViPh-Crosslinker is 95.6% and the molecular weight is 3281.

DOC (%) of ViPh-Crosslinker =

$$\frac{D^1 + D^{1'} + 2D^2 + 2D^{2'}}{2\left(D^0 + D^1 + D^{2'} + D^2 + D^{2'}\right)} \times 100 \qquad (S3-1)$$

Molecular weight of ViPh-Crosslinker =

$$\frac{2\left[(D^1 + D^2) \cdot M_{DPSD} + (D^{1'} + D^{2'}) \cdot M_{DMVS}\right]}{D^1 + D^{1'}} \qquad (S3-2)$$

M_{DPSD} (-Ph_2Si-O-) = 198.3g/mol, M_{DMVS} (-MeViSi-O-) = 86.1g/mol.

The **MALDI-TOF** result of ViPh-Crosslinker **(Fig. S2 (d) and Table S4)** shows that the m/z peaks, 1374.7, 1658.9, 1942.9, 2227.0 and 2510.7 perfectly match the proposed molecular formula combined with Na^+ for x of 4, 5, 6, 7 and 8 respectively. In Table S4, the results show that most of the peaks of ViPh-Crosslinker correspond to linear polymers, but there are some peaks correspond to cyclosiloxanes (~13.5%, marked with red * in Fig. S2 (d)), which are from 3:3 to 8:8 macrocyclic structures. Combining with the MALDI-TOF results of Vi-ViPh-Crosslinker (Fig. S2 (e), Table S5), it shows that these cyclosiloxanes disappeared due to the ring-opening and end-capping reaction.

Characterization of Vi-ViPh-Crosslinker:

Vi-ViPh-Crosslinker was prepared as mentioned in scheme 1(c) by further end-capping reaction conducted by ViPh-Crosslinker. The molecular structure of Vi-ViPh-Crosslinker was confirmed by FT-IR (Fig. 1(b)) and ^{29}Si-NMR (Fig. 1(d)).

In the **FT-IR spectra (Fig. 1(b))** of Vi-ViPh-Crosslinker, the silanols (peak at 3620 cm^{-1}, Si-OH) of -Ph_2Si-OH and -MeViSi-OH remained obviously weaker than that of ViPh-Crosslinker, indicating that the end-capping reaction does reduce the existence of -OH groups.

In the **^{1}H-NMR spectra (Fig. S1 (d)** and **Table S2),** the peaks at 7.1~7.7ppm, 5.8~6.15ppm and 0.0~0.3ppm can be assigned to H atoms in –Si-C_6H_5, - Si-CH=CH_2 and - Si-CH_3 groups of Vi-ViPh-Crosslinker, respectively. The molar ratio of "-Ph"：“-CH_3”：“-CH=CH_2” is 1.79：1.21：1.00，which is consistent with the expected structure (Scheme 1(c)). The integral peak area ratio is shown in **Table S3**.

In the **^{29}Si-NMR (Fig. 1(d))** of Vi-ViPh-Crosslinker, comparing to the result of ViPh-Crosslinker, the peaks of $D^{1'}$ species (-27.4 to -27.8 ppm, assigned to Si of -MeViSi-OH) and D^1 species (-39.8 to -40.2 ppm, assigned to Si of -Ph_2Si-OH) are significantly weakened, and the end-capped characteristic peaks assigned to Si of -Me_2Si-Vi appear at M^1 (-1.4 to -1.8 ppm) and $M^{1'}$ (-2.7 to -3.1 ppm). The DOC, degree of end-capping and average molecular weight of Vi-ViPh-Crosslinker can be calculated according to eqn (S4-1), (S4-2) and (S4-3) respectively (presents in Table 1). The results show that the DOC of the Vi-ViPh-Crosslinker is 97.4%, the end-capping ratio is 73.9% and its average molecular weight is 1493 (Table 1).

DOC (%) of Vi-ViPh-Crosslinker =

$$\frac{D^1 + D^{1'} + 2D^2 + 2D^{2'} + M^1 + M^{1'}}{2\left(D^0 + D^1 + D^{2'} + D^2 + D^{2'}\right) + M^1 + M^{1'}} \times 100 \qquad (S4-1)$$

Molecular weight of Vi-ViPh-Crosslinker =

$$\frac{2\left[(M^1 + M^{1'}) \cdot M_{ViMM} + (D^1 + D^2) \cdot M_{DPSD} + (D^{1'} + D^{2'}) \cdot M_{DMVS}\right]}{M^1 + M^{1'} + D^1 + D^{1'}} \qquad (S4-2)$$

End-capping ratio (%) of Vi-ViPh-Crosslinker =

$$\frac{M^1 + M^{1'}}{D^1 + M^1 + M^{1'}} \times 100 \qquad (S4-3)$$

M_{DPSD} (-Ph_2Si-O-) = 198.3g/mol, M_{DMVS} (-MeViSi-O-) = 86.1g/mol and M_{ViMM} (-$O_{1/2}$-Me_2Si-Vi) = 93.2 g/mol. In addition, M_{DPSD} and M_{DMVS} are the molar molecular weights of the repeating unit formed after the copolymerization reaction.

The results of **MALDI-TOF** spectra **of** Vi-ViPh-Crosslinker are shown in **Fig. S2 (e)** and **Table S5**, and the peak assignments of Vi-ViPh-Crosslinker are listed in Table S5. By comparison, it is found that the peak shifts perfectly match the proposed molecular formula combined with Na^+, which generally agrees with the results from FT-IR, ^{1}H-NMR and ^{29}Si-NMR. In **Table S5,** there is no peak attributed to the macrocycle among the 37 main peaks (marked with *), which indicates that the macrocycle in ViPh-Crosslinker undergo ring-opening and end-capping reaction in the further reaction progress. All the peaks can be corresponded to linear polysiloxane.

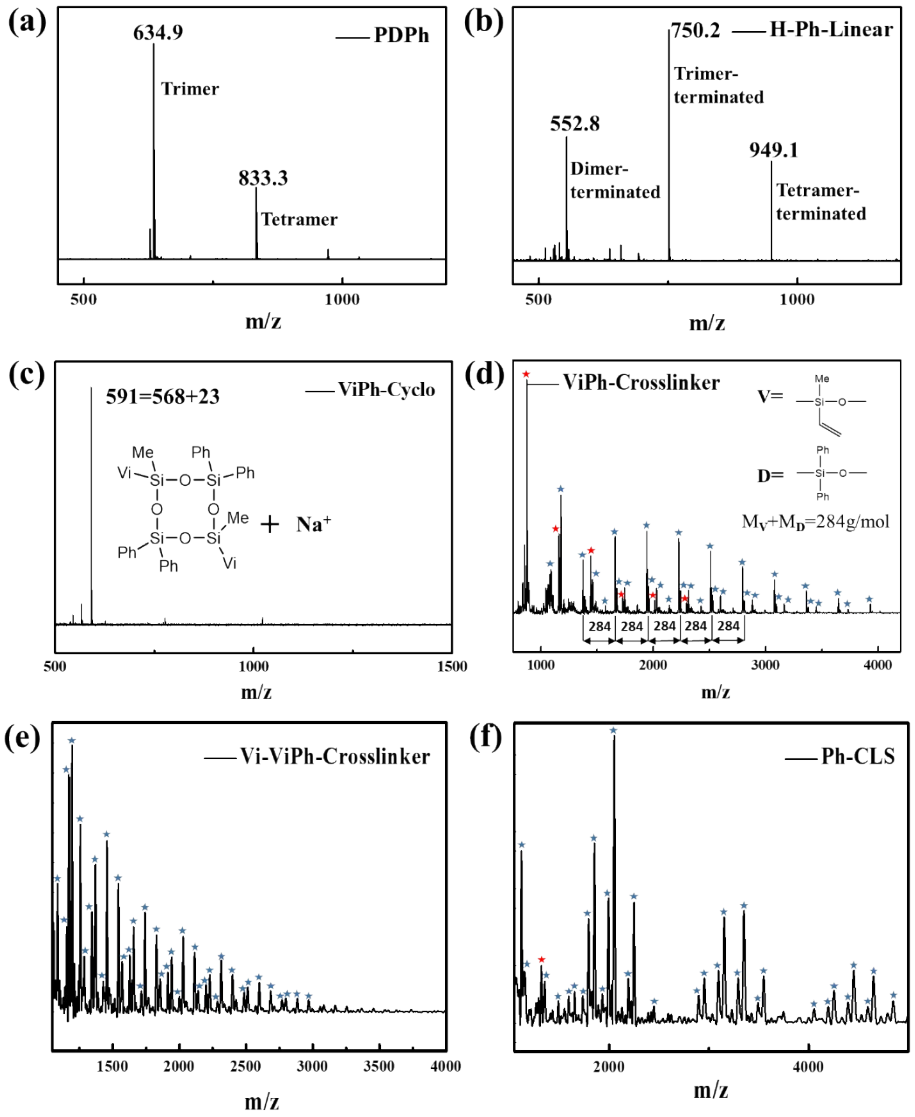
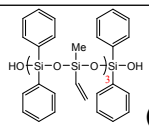
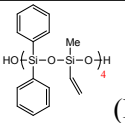
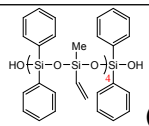
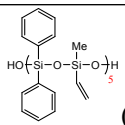
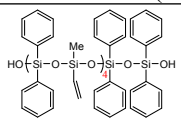
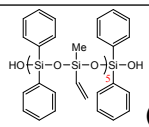
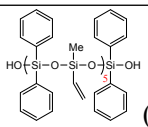
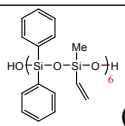
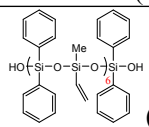
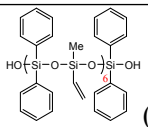
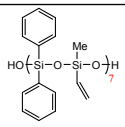
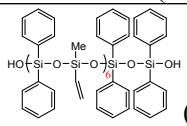
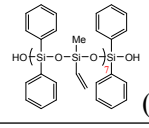
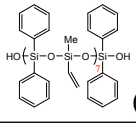
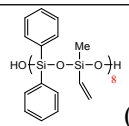
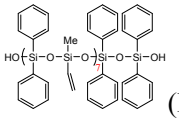
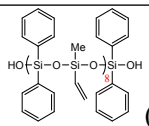
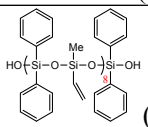
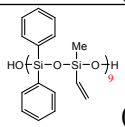
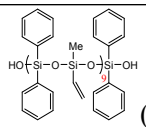
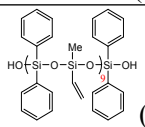
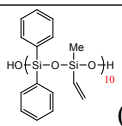
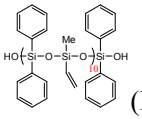
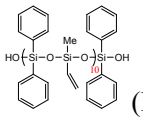
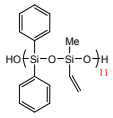
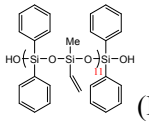
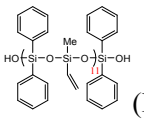
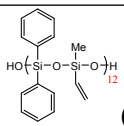


Fig. S2 MALDI-TOF results and analysis of PDPh (a), H-Ph-Linear (b), ViPh-Cyclo (c), ViPh-Crosslinker (d) Vi-ViPh-Crosslinker (e) and Ph-CLS (f). (In (d), (e) and (f), the assignments of peaks marked with * were shown in Table S4, Table S5 and Table S6, respectively)

Table S4 Peak assignment in MALDI-TOF spectrum of ViPh-Crosslinker.

Peak position	Peak intensity	Peak assignment
874.6	3001	3:3 cyclosiloxane ($M+Na^+-H^+$)
1090.6	560	 ($M+Na^+$)
1158.7	1018	4:4 cyclosiloxane ($M+Na^+-H^+$)
1177.8	1511	 ($M+Na^+$)

1374.7	684	 (M+Na$^+$)
1442.6	738	5:5 cyclosiloxane (M+Na$^+$-H$^+$)
1460.6	431	 (M+Na$^+$)
1572.9	93	 (M+Na$^+$)
1658.9	988	 (M+Na$^+$)
1674.4	318	 (M+K$^+$-H$^+$)
1726.8	197	6:6 cyclosiloxane (M+Na$^+$-H$^+$)
1744.9	325	 (M+Na$^+$)
1942.9	1050	 (M+Na$^+$)
1958.3	341	 (M+K$^+$-H$^+$)
2010.4	164	7:7 cyclosiloxane (M+Na$^+$-H$^+$)
2028.6	317	 (M+Na$^+$-H$^+$)
2140.6	106	 (M+Na$^+$-H$^+$)
2227.0	957	 (M+Na$^+$)
2242.5	286	 (M+K$^+$-H$^+$)
2294.8	129	8:8 cyclosiloxane (M+Na$^+$-H$^+$)

2312.6	295	 (M+Na$^+$-H$^+$)
2424.8	91	 (M+Na$^+$-H$^+$)
2510.7	788	 (M+Na$^+$-H$^+$)
2528.0	231	 (M+K$^+$-H$^+$)
2597.1	215	 (M+Na$^+$)
2794.5	597	 (M+Na$^+$-H$^+$)
2810.4	161	 (M+K$^+$-H$^+$)
2880.1	168	 (M+Na$^+$-H$^+$)
3078.9	425	 (M+Na$^+$-H$^+$)
3095.1	116	 (M+K$^+$-H$^+$)
3163.7	119	 (M+Na$^+$-H$^+$)
3363.0	287	 (M+Na$^+$-H$^+$)
3378.8	80	 (M+K$^+$-H$^+$)
3448.7	82	 (M+ Na$^+$-H$^+$)

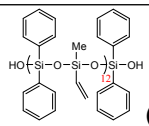
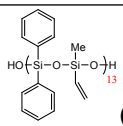
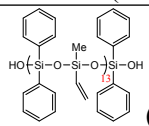
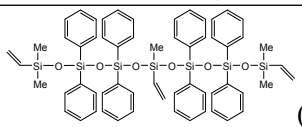
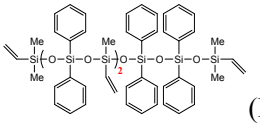
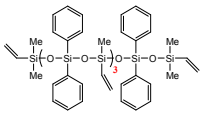
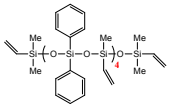
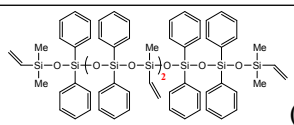
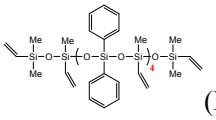
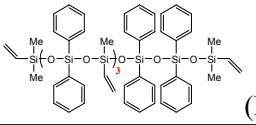
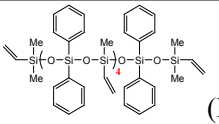
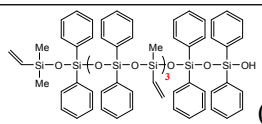
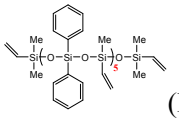
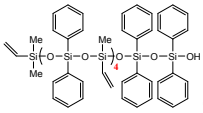
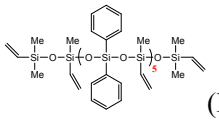
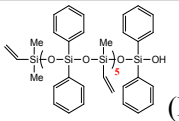
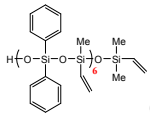
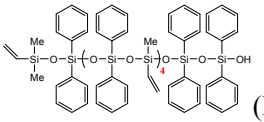
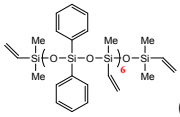
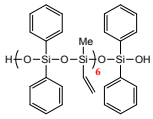
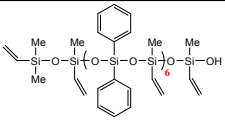
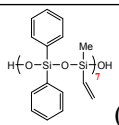
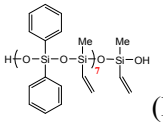
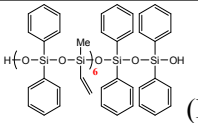
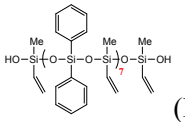
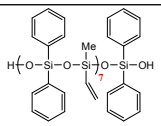
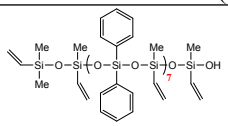
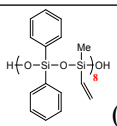
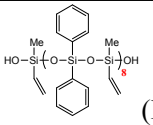
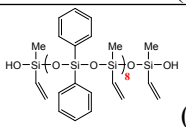
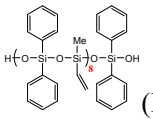
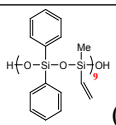
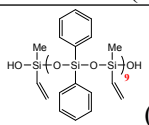
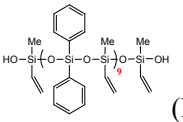
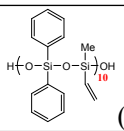
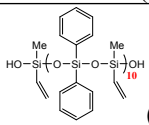
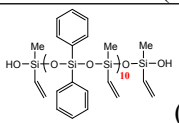
3647.2	191	 (M+Na$^+$)
3732.6	49	 (M+ Na$^+$-H$^+$)
3931.1	118	 (M+Na$^+$)

Table S5 Peak assignment in MALDI-TOF spectrum of Vi-ViPh-Crosslinker.

Peak position	Peak intensity	Peak assignment
1087.5	21521	 (M+Na$^+$)
1156.6	14219	-
1172.7	39764	 (M+Na$^+$-H$^+$)
1196.1	44620	-
1257.8	31395	 (M+Na$^+$-H$^+$)
1286.8	9367	-
1344.1	16787	 (M+Na$^+$-H$^+$)
1371.2	24694	 (M+Na$^+$)
1429.8	5123	 (M+Na$^+$-H$^+$)
1457.7	28666	 (M+Na$^+$)
1543.0	21514	 (M+Na$^+$)

1571.3	8434	 (M+Na$^+$)
1629.1	9539	 (M+Na$^+$)
1657.2	14244	 (M+Na$^+$)
1714.2	3528	 (M+Na$^+$-H$^+$)
1743.0	16737	 (M+Na$^+$)
1828.8	12925	 (M+Na$^+$)
1856.4	5561	 (M+Na$^+$-H$^+$)
1913.9	6653	 (M+Na$^+$)
1942.9	9192	 (M+Na$^+$)
2000.3	2568	 (M+Na$^+$-H$^+$)
2028.3	12645	 (M+Na$^+$-H$^+$)
2114.0	9983	 (M+Na$^+$-H$^+$)
2141.4	3625	 (M+Na$^+$)
2199.8	4613	 (M+Na$^+$-H$^+$)

2227.4	6253	 (M+Na$^+$)
2284.7	1823	 (M+Na$^+$-H$^+$)
2313.4	8647	 (M+Na$^+$)
2399.5	6232	 (M+Na$^+$)
2484.2	3251	 (M+Na$^+$-H$^+$)
2511.8	4195	 (M+Na$^+$)
2598.2	4949	 (M+Na$^+$)
2684.2	3545	 (M+Na$^+$)
2769.4	2052	 (M+Na$^+$)
2797.5	2333	 (M+Na$^+$)
2883.4	2289	 (M+Na$^+$)
2969.1	2070	 (M+Na$^+$)

In **Table S6**, MALDI-TOF spectrum peak assignment of Ph-CLS, “L” and “C” represent precursor materials for the preparation of hydrosilylation of cyclo-linear structure, and the molecular structure is as follows.

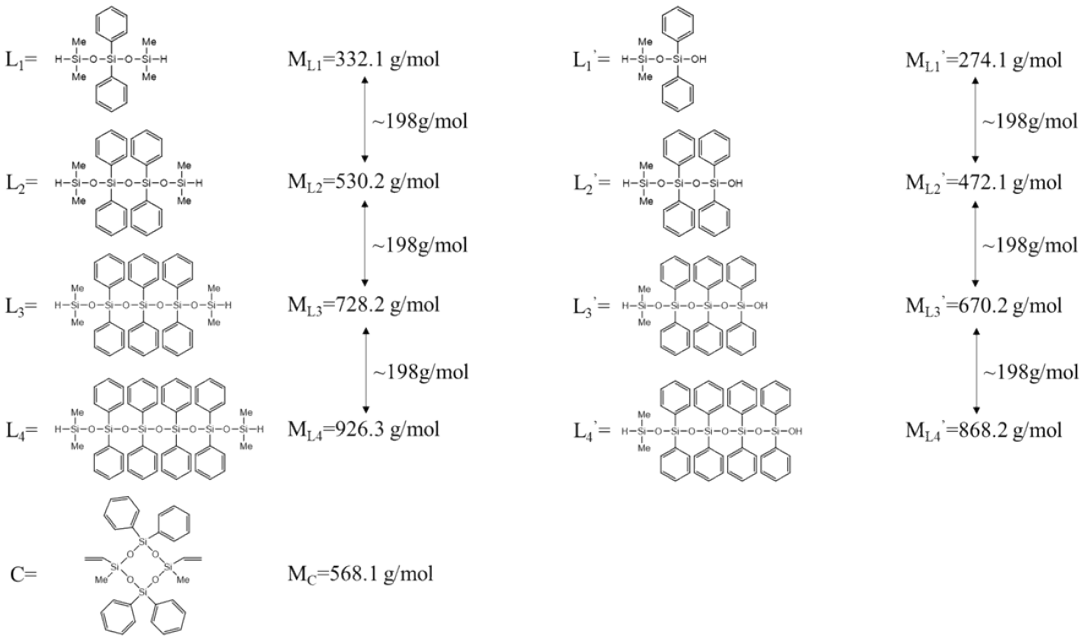


Table S6 Peak assignment in MALDI-TOF spectrum of Ph-CLS.

Peak position	**Peak intensity**	**Peak assignment**	**The ratio of "linear" and "cyclo" contained in the molecular chain or macrocycle.**
1119.1	8976	-	-
1149.2	2690	-	-
1318.5	3012	(L_3+C) (M+Na^+)	1:1 (linear or macrocycle)
1352.4	2181	-	-
1488.7	1167	-	-
1594.1	1402	(L_2 +L_2'+C) (M+Na^+)	2:1(linear)
1652.5	1651	(2L_2+C) (M+Na^+)	2:1(linear)
1734.8	1427	(L_2'+L_3'+C) (M+Na^+)	2:1(linear)
1792.6	5449	(L_2+ L_3'+C) (M+Na^+)	2:1(linear)
1850.9	9388	(L_2+ L_3+C) (M+Na^+)	2:1(linear)
1932.3	1544	(2L_3'+C) (M+Na^+)	2:1(linear)
1991.1	6537	(L_3+ L_3'+C) (M+Na^+)	2:1(linear)
2049.5	15014	(2L_3+C) (M+Na^+)	2:1(linear)
2189.4	2335	(L_3+ L_4'+C) (M+Na^+)	2:1(linear)
2248.3	6314	(L_3+ L_4+C) (M+Na^+)	2:1(linear)

2446.5	893	$(2L_4+C)$ $(M+Na^+)$	2:1(linear)
2896.6	1456	$(2L_2+ L_3'+2C)$ $(M+Na^+)$	3:2(linear)
2953.9	2354	$(2L_2+ L_3+2C)$ $(M+Na^+)$	3:2(linear)
3095.1	2752	$(L_2'+ 2L_3+2C)$ $(M+Na^+)$	3:2(linear)
3153.3	5541	$(L_2+ 2L_3+2C)$ $(M+Na^+)$	3:2(linear)
3292.8	2362	$(2L_3+ L_3'+2C)$ $(M+Na^+)$	3:2(linear)
3351.7	5887	$(3L_3+2C)$ $(M+Na^+)$	3:2(linear)
3492.2	1074	$(2L_3+ L_4'+2C)$ $(M+Na^+)$	3:2(linear)
3550.3	2463	$(2L_3+ L_4+2C)$ $(M+Na^+)$	3:2(linear)
4054.0	751	$(3L_2 + L_3+3C)$ $(M+Na^+)$	4:3(linear)
4197.3	864	$(2L_2+ L_3+ L_3'+3C)$ $(M+Na^+)$	4:3(linear)
4255.0	1711	$(2L_2+ 2L_3+3C)$ $(M+Na^+)$	4:3(linear)
4396.3	1094	$(L_2+2L_3+L_3'+3C)$ $(M+Na^+)$	4:3(linear)
4453.7	2767	$(L_2+ 3L_3+3C)$ $(M+Na^+)$	4:3(linear)
4594.3	869	$(3L_3+L_3'+3C)$ $(M+Na^+)$	4:3(linear)
4652 .3	2461	$(4L_3+3C)$ $(M+Na^+)$	4:3(linear)
4849.1	1163	$(3L_3+ L_4+3C)$ $(M+Na^+)$	4:3(linear)

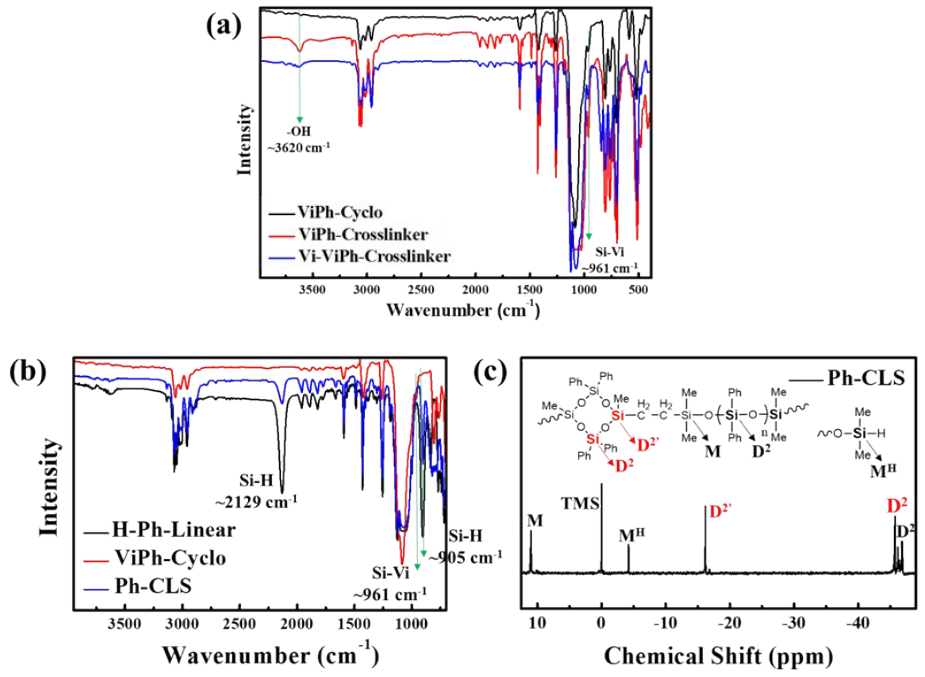


Fig. S3 (a) FT-IR spectra of ViPh-Cyclo, ViPh-Crosslinker and Vi-ViPh-Crosslinker. (b) FT-IR

spectra of H-Ph-Linear, ViPh-Cyclo and Ph-CLS. (c) The ^{29}Si-NMR spectrum of Ph-CLS.

Table S7 The molar ratio of precursors of "H-Ph-Linear/ViPh-Cyclo", "H-Ph-Linear/Vi-ViPh-Crosslinker" and "H-Ph-Linear/ViPh-Cyclo/Vi-ViPh-Crosslinker".

	H-Ph-Linear (Si-H)	**ViPh-Cyclo (Si-Vi)**	**Vi-ViPh-Crosslinker (Si-Vi)**
"H-Ph-Linear/ViPh-Cyclo"	4	3	
"H-Ph-Linear/Vi-ViPh-Crosslinker"	4		1
"H-Ph-Linear/ViPh-Cyclo/Vi-ViPh-Crosslinker"	4	3	1

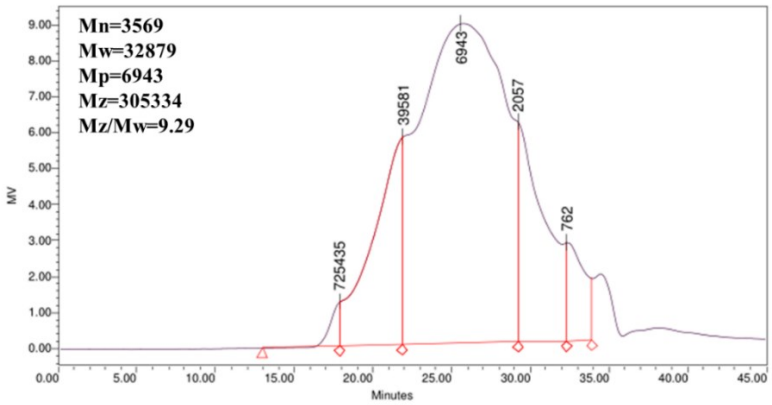


Fig. S4 GPC result of Ph-CLS.

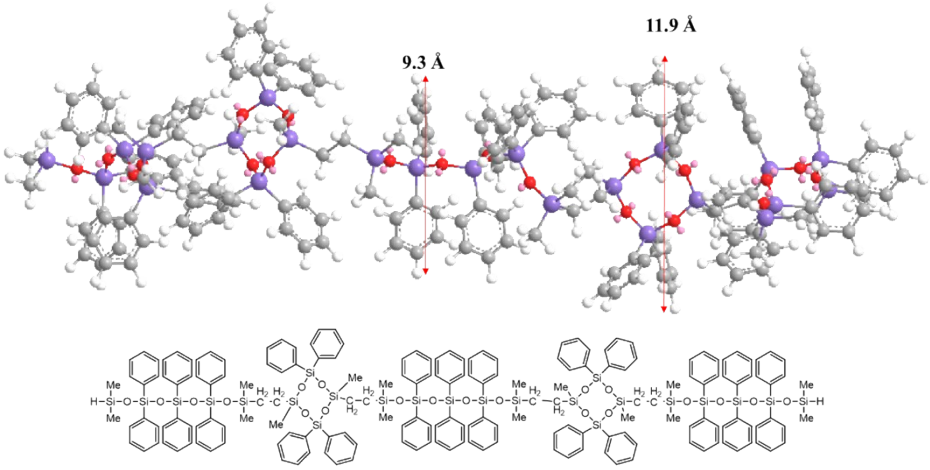


Fig. S5 The molecular simulation result of the cyclo-linear siloxane Ph-CLS with two repeat unit. (The chemical structures were drawn by ChemDraw Ultra 12.0)

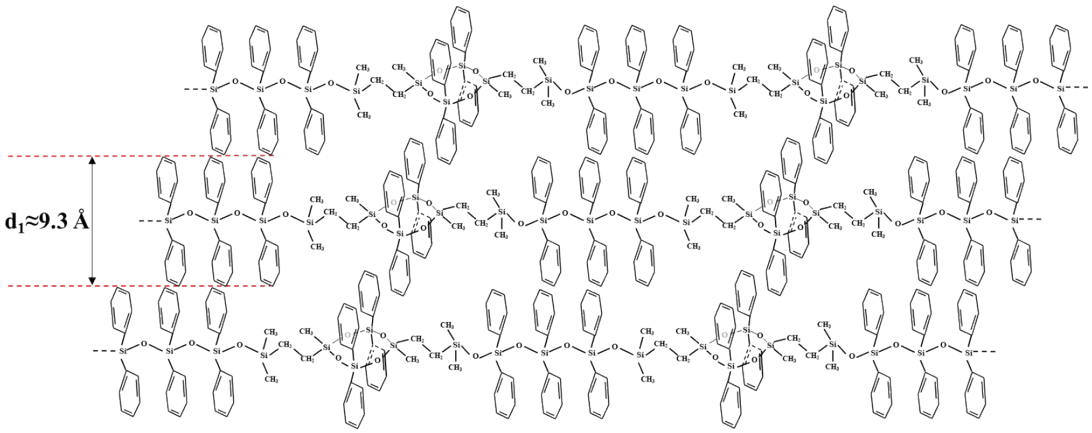


Fig. S6 The proposed chain arrangement corresponding to the XRD results.

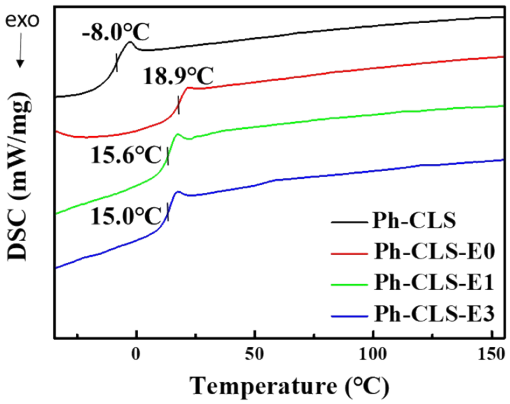
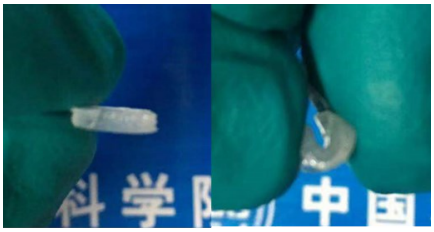


Fig. S7 DSC curves of Ph-CLS/Ph-CLS-Es.



Ph-CLS-E3

Fig. S8 Schematic diagram of bending sample of Ph-CLS-E3.