Electronic Supplementary information

Silicone elastomers with covalently incorporated aromatic voltage stabilizers

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1) Number of PDMS-PPMS repeating units and stoichiometric ratio of cross-linked PDMS-PPMS copolymers

The targeted number of PDMS-PPMS repeating units in the copolymer (X) was calculated such that the targeted $M_{n,T}$ results in a telechelic hydride terminated PDMS-PPMS copolymer as shown below:

$$X = \frac{M_{n,T} - M_{n,PPMS}}{M_{n,PDMS} + M_{n,PPMS}}$$

Equation 1

where $M_{n,PDMS}$ and $M_{n,PPMS}$ are the molecular weight of PDMS and PPMS, respectively.

The stoichiometric ratio for preparing telechelic hydride-functional PDMS-PPMS copolymers (r_1) was calculated as:

$$r_1 = \frac{[hydride]}{[vinyl]} = \frac{(X+1)f_{PPMS}}{Xf_{PDMS}} = \frac{X+1}{X}$$

Equation 2

where f_{PDMS} and f_{PPMS} are the functionality of PDMS (f_{PDMS} = 2) and PPMS (f_{PPMS} = 2), respectively.

2) Stoichiometric ratio of crosslinking

The stoichiometric ratio for the cross-linking (r_2) was 1.5 and was calculated below:

$$r_2 = \frac{[vinyl]}{[hydride]} = \frac{F_{CL}[CL]_0}{F_{CP}[CP]_0} = \frac{F_{CL}}{F_{CP}} \cdot \frac{m_{CL}/M_{CL}}{m_{CP}/M_{CP}}$$

Equation 3

where F_{CL} and F_{CP} are average numbers of functional group on the crosslinker (15-functional) and the PDMS-PPMS copolymer (2-functional), respectively, while $[\ldots]_0$, m_x, and M_x are the initial concentration, the mass and the molecular weight, respectively, (x = *CL*, *CP*).

3) Calculation of molar concentration of phenyl groups in PDMS-PPMS elastomers from ^{1}H-NMR

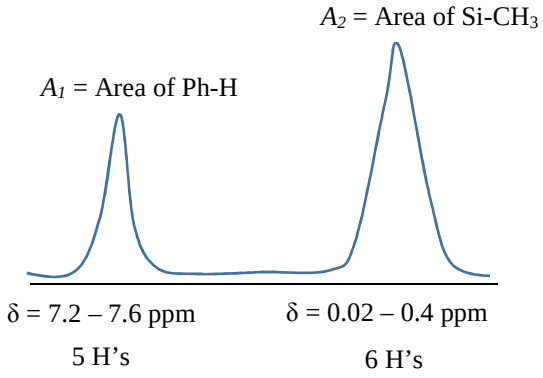


Figure S1 The illustration of NMR spectrum with peaks of phenyl and methyl of PDMS-PPMS elastomer.

a) Relative number of moles of phenylmethylsiloxane (X_1):
Note: The proton signal at δ = 7.2 – 7.6 ppm representing the phenyl (C_6H_5) protons (5H's).

$$X_1 = \frac{A_1}{H_1}$$

Equation 4

where A_1 and H_1 are the area of integration and the number of protons for phenyl group, respectively.

b) Relative number of moles of dimethylsiloxane (X_2):
Note: The proton signal at δ = 0.02 – 0.4 ppm representing the dimethyl [$(CH_3)_2$] protons (6H's).

$$X_2 = \frac{A_2 - Me(end) - Me(PMS)}{H_2} = \frac{A_2 - 12X_1 - 3m \cdot X_1}{H_2}$$

Equation 5

where A_2 and H_2 are the area of integration and the number of protons for methyl, respectively, while $Me(end)$ and $Me(PMS)$ are methyl groups for telechelic hydride end-groups and phenylmethylsiloxane unit (m), respectively.

c) Actual mole percentage of phenyl groups of PDMS-PPMS elastomer ($n_{C_6H_6}$ in mol):

$$n_{C_6H_6} = \frac{X_1}{X_1 + X_2}$$

Equation 6

d) True molar concentration of phenyl groups of PDMS-PPMS elastomer ($C_{C_6H_6}$ in mol/g):

$$C_{C_6H_6} = \frac{n_{C_6H_6}}{m_{PPMS} + m_{PDMS}}$$

Equation 7

where m_{PPMS} and m_{PDMS} are masses of PPMS and PDMS, respectively.

4) Calculation of engineering stress and strain

The engineering stress (σ_E) was calculated from the force (*F*) and the cross-sectional area of the strip (*A*):

$$\sigma_E = \frac{F}{A} = \frac{F}{t \times w} = \frac{\tau \cdot d}{t \cdot w}$$

Equation 8

where *A* = film thickness (t) · constant width (w = 6 mm) and *F* = torque (τ) · drum diameter (d = 10.3 mm).

The engineering strain (ϵ_E) was calculated as a ratio of a stretched strain ($L - L_0$) to an initial strain (L_0) as:

$$\epsilon_E = \frac{L - L_0}{L_0}$$

Equation 9

where a final strain after stretching (L) was determined from Hencky strain (ϵ_H) as follows:

$$\epsilon_H = ln\frac{L}{L_0}$$

Equation 10

$$L = L_0 e^{\epsilon_H} = L_0 e^{(r_H)t_s}$$

Equation 11

where ϵ_H is a product of Hencky rate (r_H = 1×10^{-3} rotation/s) and step time (t_s).

By putting equation (11) in (9), the final expression of engineering strain (ϵ_E) was obtained as below:

$$\epsilon_E = e^{\epsilon_H} - 1$$

Equation 12

Young's moduli were determined from slopes in the linear regime of stress-strain plots at 5 % strain.

5) NMR spectra of PDMS-PPMS copolymers

The NMR spectra for PDMS-PPMS copolymers with different true molar concentrations of phenyl groups ($C_{C_6H_6}$) are shown in Figures S2– S9.

a) PDMS-PPMS copolymer (**377DMS_2PMS**, $C_{C_6H_6}$ = 5.0 × 10^{-4} mol g^{-1})

^{1}H-NMR ($CDCl_3$, 300 MHz): δ -0.02 - δ 0.6 (m, 6 H's, -SiO(C**H$_3$)$_2$**-), δ 4.70 (m, 1 H, -Si**H**-), δ 7.10 - δ 7.60 (m, 5 H's, -SiC$_6$**H$_5$**-).

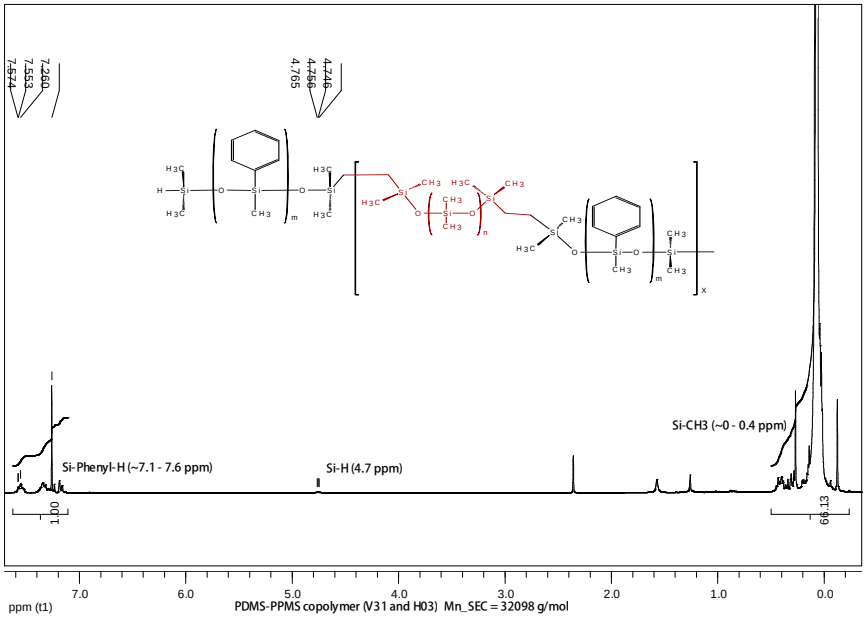


Figure S2 The NMR for 377DMS_2PMS.

b) PDMS-PPMS copolymer (**231DMS_2PMS**, $C_{C_6H_6}$ = 6.9 × 10^{-4} mol g^{-1})

^{1}H-NMR ($CDCl_3$, 300 MHz): δ -0.02 - δ 0.6 (m, 6 H's, -SiO(C**H$_3$)$_2$**-), δ 4.70 (m, 1 H, -Si**H**-), δ 7.10 - δ 7.60 (m, 5 H's, -SiC$_6$**H$_5$**-).

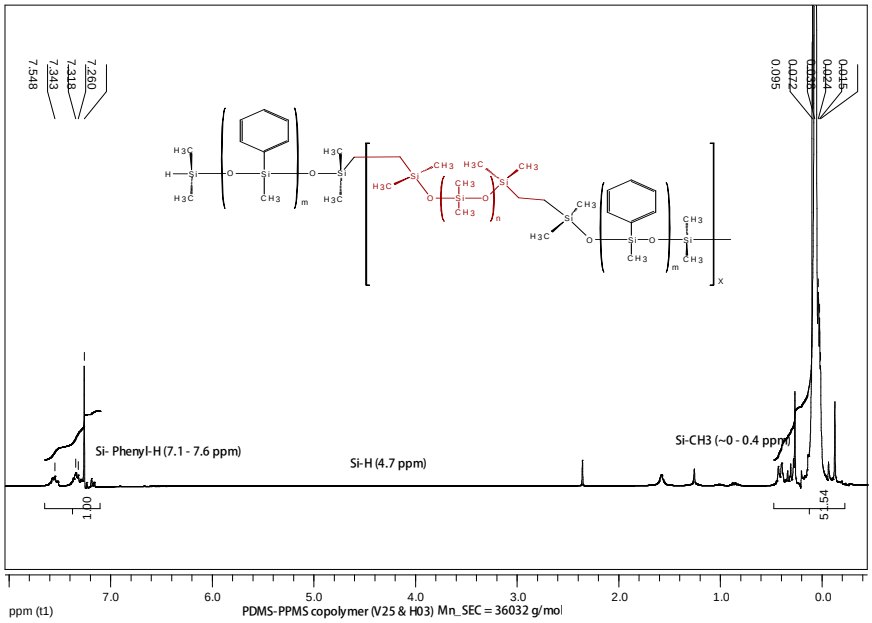


Figure S3 The NMR for 231DMS_2PMS.

c) PDMS-PPMS copolymer (**126DMS_2PMS**, $C_{C_6H_6}$ = 7.8 × 10^{-4} mol g^{-1})

^{1}H-NMR ($CDCl_3$, 300 MHz): δ -0.02 - δ 0.6 (m, 6 H's, -SiO(C**H$_3$)$_2$**-), δ 4.70 (m, 1 H, -Si**H**-), δ 7.10 - δ 7.60 (m, 5 H's, -SiC$_6$**H$_5$**-).

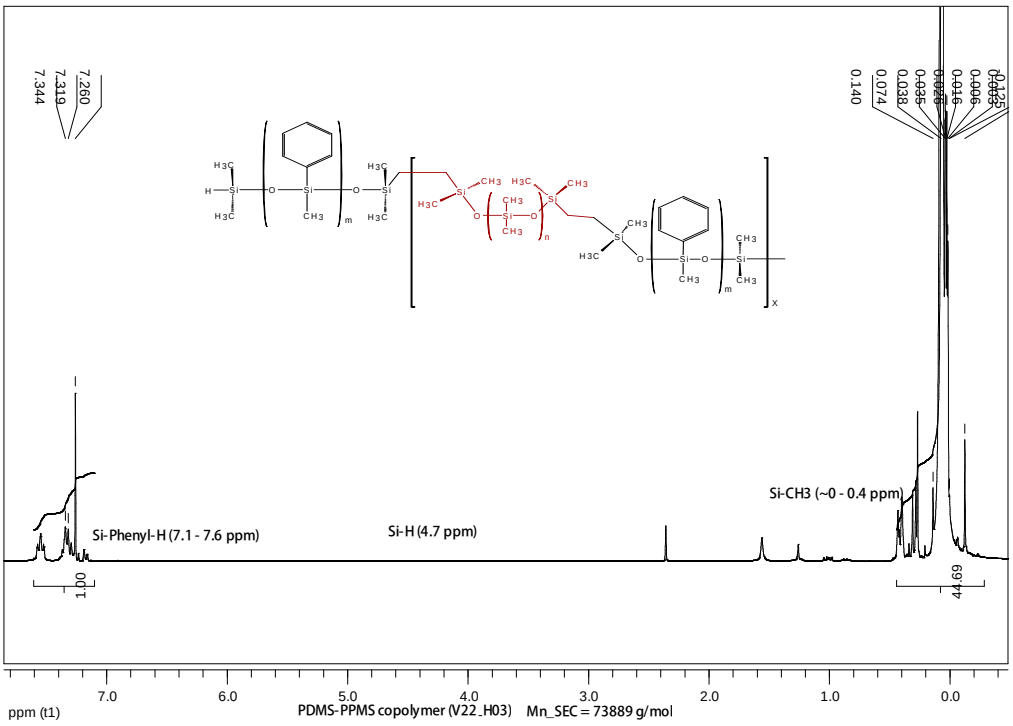


Figure S4 The NMR for 126DMS_2PMS.

d) PDMS-PPMS copolymer (**80DMS_2PMS**, $C_{C_6H_6}$ = 8.4 × 10^{-4} mol g^{-1})

^{1}H-NMR ($CDCl_3$, 300 MHz): δ -0.02 - δ 0.6 (m, 6 H's, -SiO(C**H$_3$)$_2$**-), δ 4.70 (m, 1 H, -Si**H**-), δ 7.10 - δ 7.60 (m, 5 H's, -SiC$_6$**H$_5$**-).

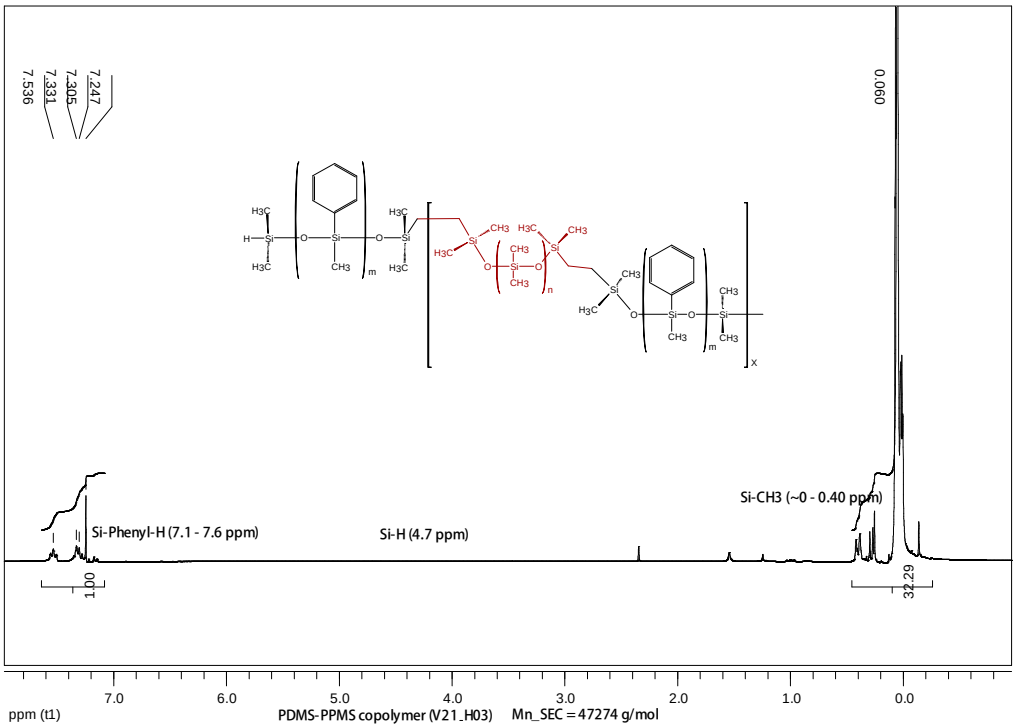


Figure S5 The NMR for 80DMS_2PMS.

e) PDMS-PPMS copolymer (**377DMS_6PMS**, $C_{C_6H_6}$ = 8.7 × 10^{-4} mol g^{-1})

^{1}H-NMR ($CDCl_3$, 300 MHz): δ -0.02 - δ 0.6 (m, 6 H's, -SiO(C**H$_3$)$_2$**-), δ 4.70 (m, 1 H, -Si**H**-), δ 7.10 – δ 7.60 (m, 5 H's, -SiC$_6$**H$_5$**-).

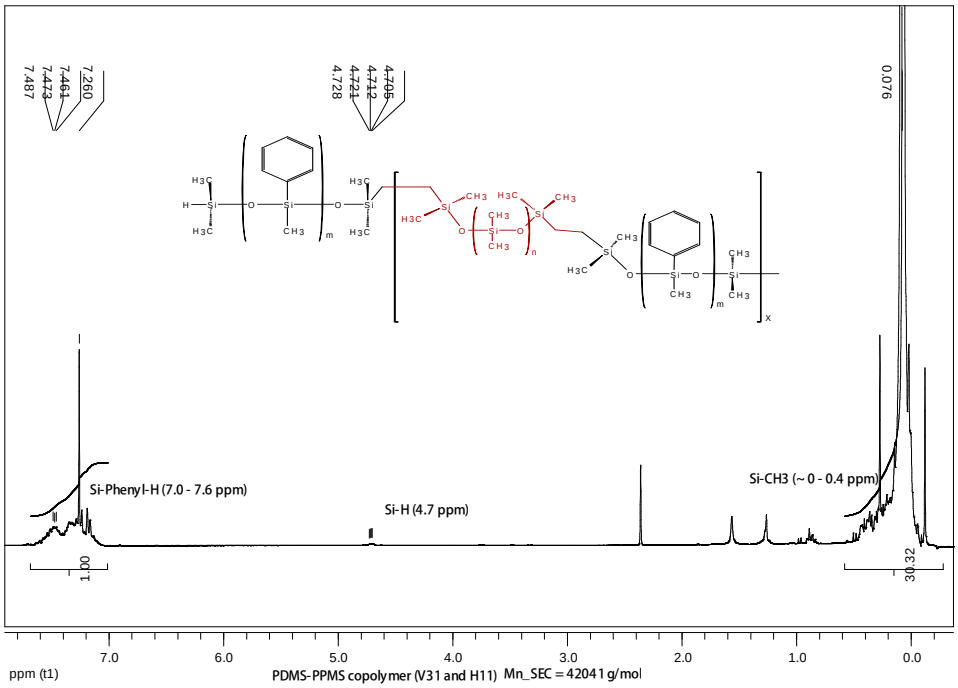


Figure S6 The NMR for 377DMS_6PMS.

f) PDMS-PPMS copolymer (**231DMS_6PMS**, $C_{C_6H_6}$ = 9.8 × 10^{-4} mol g^{-1})

^{1}H-NMR ($CDCl_3$, 300 MHz): δ -0.02 - δ 0.6 (m, 6 H's, -SiO(C**H$_3$)$_2$**-), δ 4.70 (m, 1 H, -Si**H**-), δ 7.10 - δ 7.60 (m, 5 H's, -SiC$_6$**H$_5$**-).

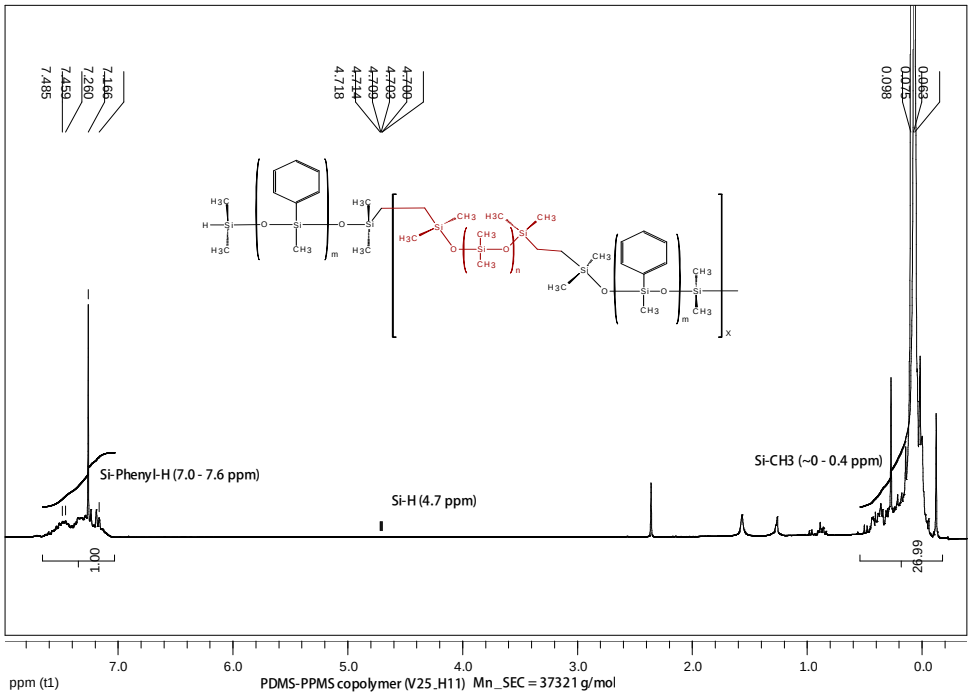


Figure S7 The NMR for 231DMS_6PMS.

g) PDMS-PPMS copolymer (**126DMS_6PMS**, $C_{C_6H_6}$ = 1.5 × 10^{-3} mol g^{-1})

^{1}H-NMR ($CDCl_3$, 300 MHz): δ -0.02 - δ 0.6 (m, 6 H's, -SiO(C**H$_3$)$_2$**-), δ 4.70 (m, 1 H, -Si**H**-), δ 7.10 - δ 7.60 (m, 5 H's, -SiC$_6$**H$_5$**-).

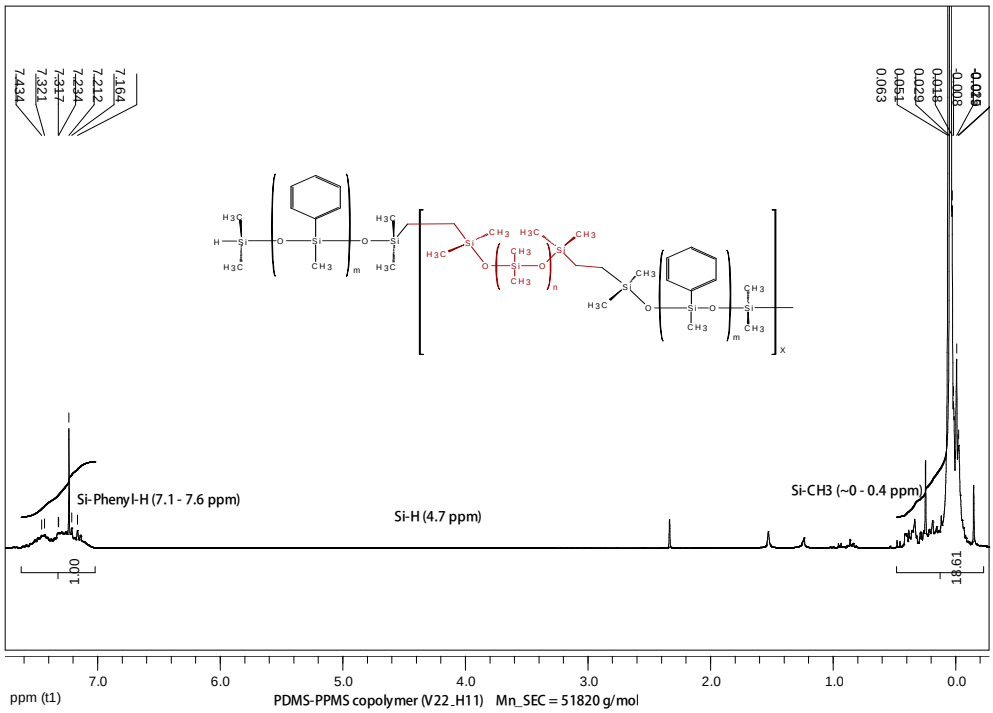


Figure S8 The NMR for 126DMS_6PMS.

h) PDMS-PPMS copolymer (**80DMS_6PMS**, $C_{C_6H_6}$ = 2.0 × 10^{-3} mol g^{-1})

^{1}H-NMR ($CDCl_3$, 300 MHz): δ -0.02 - δ 0.6 (m, 6 H's, -SiO(C**H$_3$)$_2$**-), δ 4.70 (m, 1 H, -Si**H**-), δ 7.10 - δ 7.60 (m, 5 H's, -SiC$_6$**H$_5$**-).

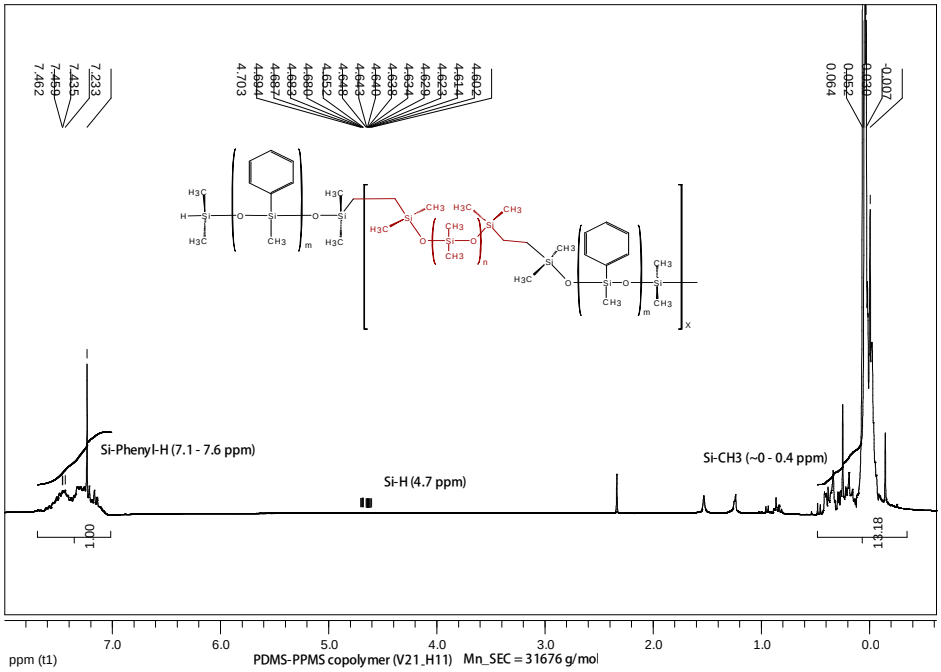
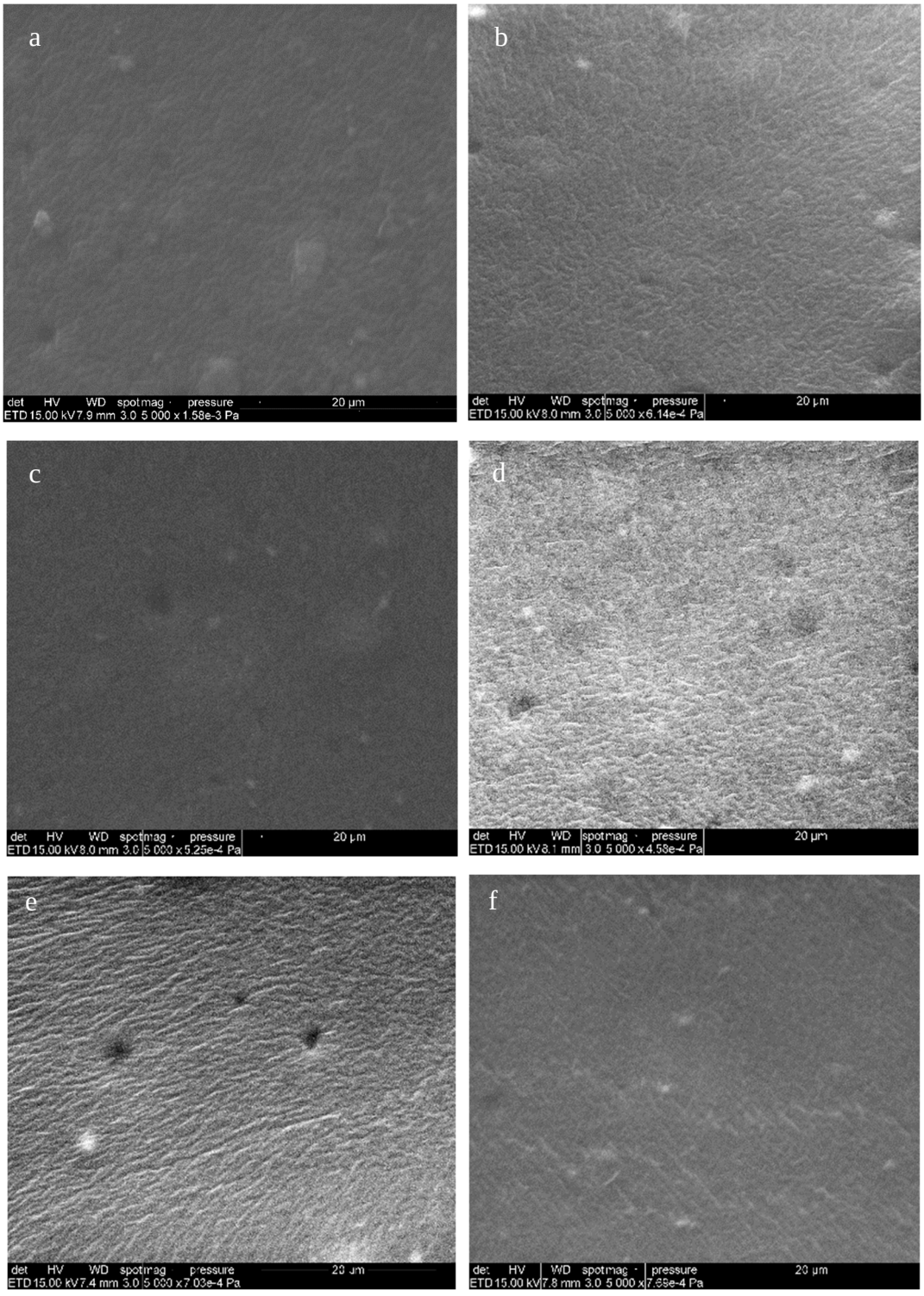


Figure S9 The NMR for 80DMS_6PMS.

6) Scanning electron microscopy (SEM) images for the cross-linked copolymers and the reference



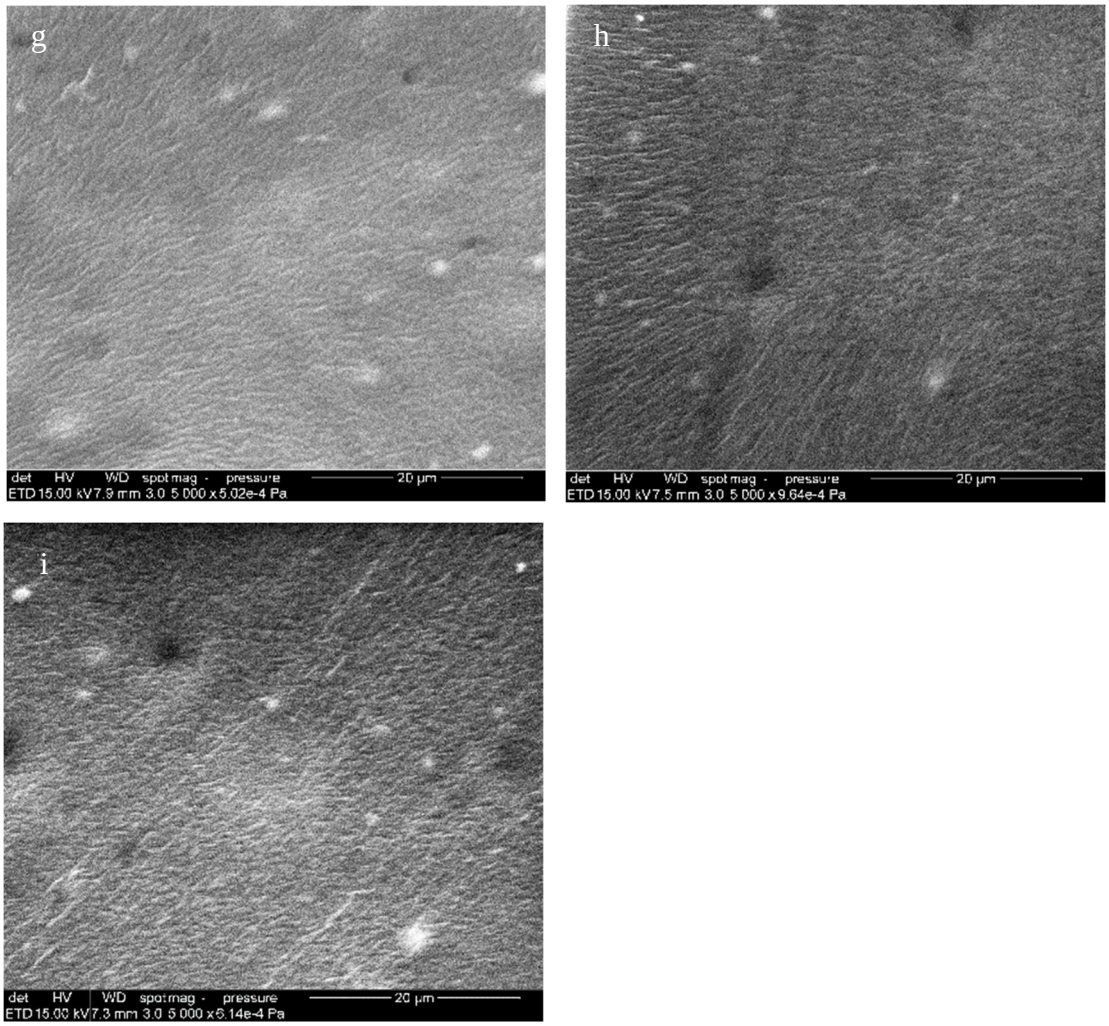


Figure S10 SEM images of: **a**) DMS-H31 (*C*=0), **b**) 377DMS_2PMS (*C*=5.0), **c**) 231DMS_2PMS (*C*=6.9), **d**) 126DMS_2PMS (*C*=7.8), **e**) 80DMS_2PMS (*C*=8.4), **f**) 377DMS_6PMS (*C*=8.7), **g**) 231DMS_6PMS (*C*=9.8), **h**) 126DMS_6PMS (*C*=15), and **i**) 80DMS_6PMS (*C*=20), *C* is in 10^{-4} g/mol.

7) Electrical breakdown strengths as function of Young's moduli for the cross-linked PDMS-PPMS copolymers and the reference elastomer

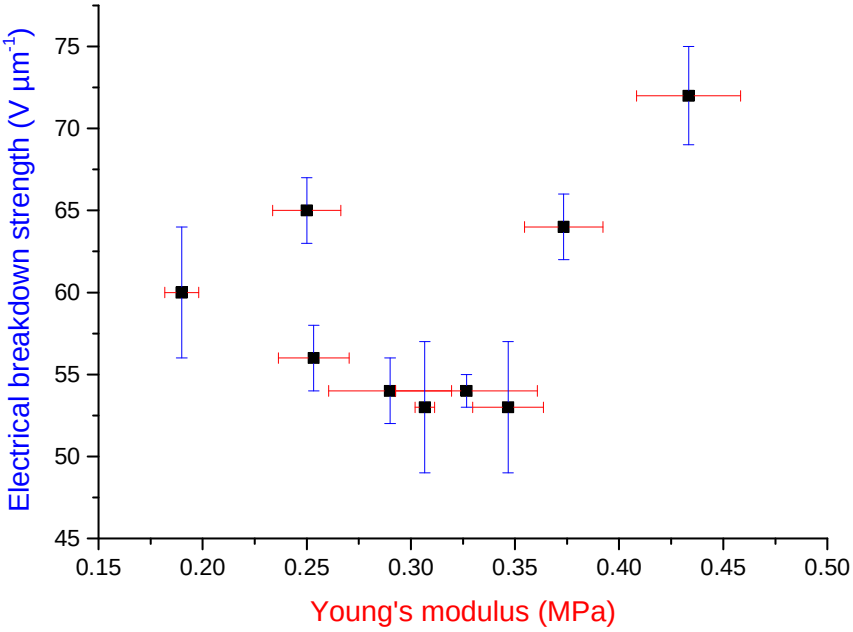


Figure S11 A plot of electrical breakdown strengths versus Young's moduli.

8) Weibull parameters η and β as function of Young's moduli for the cross-linked PDMS-PPMS copolymers and the reference elastomer

The curves of Weibull parameters η and β versus determined Young's moduli for the cross-linked copolymers and the reference are shown in Figure S12. Figure S12 (a) shows an optimum of β-parameter (60) occurring at Young's modulus of 0.33 MPa. For η-parameter, the optimum occurs at the highest Young's modulus of 0.43 MPa (see Figure S12 (b)).

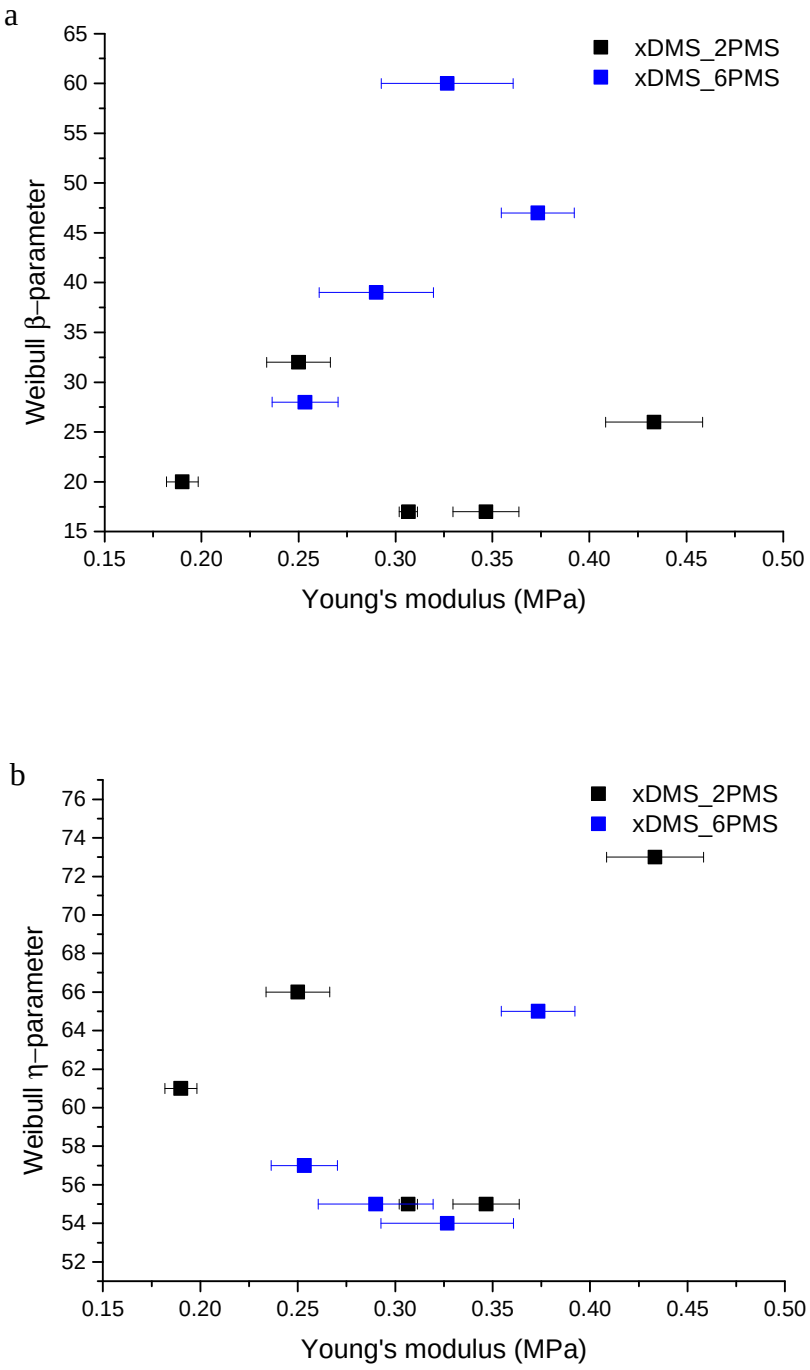


Figure S12 Weibull parameters versus Young's moduli: a) β-parameter, b) η-parameter.

9) Theoretical molar concentration of phenyl group

The numbers of phenyl groups in PPMS with $M_{n,PPMS}$ of 400 and 1000 g mol^{-1}, respectively, are given by:

$$m^* = \frac{M_{n,PPMS} - 2M_{end}}{M_{PMS}}$$

Equation 13

where M_{PMS} and M_{end} are molecular weights of phenylmethylsiloxane unit (M_{PMS} = 136 g mol^{-1}) and telechelic hydride groups, Si(CH$_3$)$_2$-H, (M_{end} = 56 g mol^{-1}), respectively. Thus a cross-linked PDMS-PPMS copolymer containing short- and long-chain PPMS are defined as m^* = 2 and 6, respectively.

The theoretical molar concentration of phenyl groups in cross-linked PDMS-PPMS copolymers C_{t,C_6H_6} in mol g^{-1} was determined as:

$$C_{t,C_6H_6} = \frac{m^* \cdot n_{PPMS}}{m_{PPMS} + m_{PDMS}} = \frac{m^* \cdot n_{PPMS}}{n_{PPMS} \cdot M_{n,PPMS} + n_{PDMS} \cdot M_{n,PDMS}}$$

Equation 14

where m_{PPMS} and m_{PDMS} are masses of PPMS and PDMS, respectively, while n_{PPMS} and n_{PDMS} are molar amounts.

The molar amount of PPMS is expressed as $n_{PPMS} = (X + 1)n_{PDMS}$ and Equation 14 can be simplified as follows:

$$C_{t,C_6H_6} = \frac{m^* \cdot (X + 1)}{(X + 1)M_{n,PPMS} + M_{n,PDMS}}$$

Equation 15

The simplified theoretical molar concentrations of phenyl group in PDMS-PPMS can be calculated below:

$$C_{t,C_6H_6} = \frac{m^*}{M_{n,PPMS} + (X + 1)^{-1}M_{n,PDMS}}$$

Equation 16

Samples with different theoretical molar concentrations of phenyl groups in PDMS-PPMS copolymer are listed in Table S1:

Table S1 Theoretical phenyl concentrations of cross-linked PDMS-PPMS copolymers.

PDMS-PPMS copolymer (*n*DMS_*m*PMS)	Theoretical molar concentration of phenyl groups C_{t,C_6H_6} [10^{-4} mol g^{-1}]
377DMS_2PMS	1.3
231DMS_2PMS	1.6
126DMS_2PMS	2.3
80DMS_2PMS	3.5
377DMS_6PMS	3.7
231DMS_6PMS	5.6
126DMS_6PMS	7.3
80DMS_6PMS	11

10) UV/Vis spectra of the cross-linked copolymers and the reference elastomer

The absorption spectra of energy from UV/Vis light absorbed by different concentrations of phenyl group are shown in Figure S13. The phenyl group of the cross-linked copolymers absorbs UV/Vis light in the energy band of 4.5 – 5.5 eV as seen from the absorbance peaks.

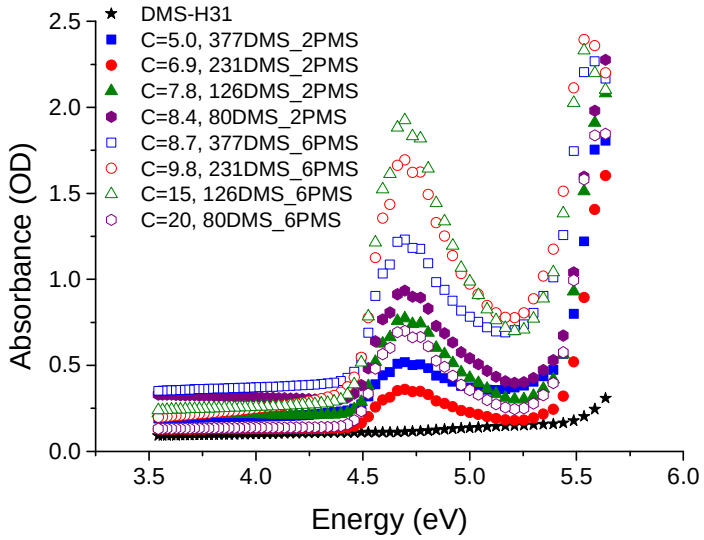


Figure S13 Spectra of UV/Vis absorption of PDMS elastomer and cross-linked PDMS-PPMS copolymers; *C* is in 10^{-4} mol g^{-1}.