

Supporting information for

Syntheses and Supramolecular Associations of New Phosphonated and Sulfoned Silicone Block and Grafted Copolymers

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Table S1. Grafting of dimethylvinyl phosphonate onto PDMS-co-PHMS polymers catalyzed by $B(C_6F_5)_3$.^a

Run	PDMS	DEVPSi-H mol/mol	Conv. %
entry 1	A	6.6	92
Entry 2	B	3.3	93
entry 3	C	3.3	78

^a Conditions : 1 eq Si-H; 0.17 eq $B(C_6F_5)_3$; m (Si-H) = m (Tol)=1 g; T = 85°C. ^b PDMS A: telechelic hydride terminated poly(dimethylsiloxane), $M_n=23,500$ g/mol; PDMS B: 5 Si-H groups/chain, $M_n=5140$ g/mol; PDMS C: 12 Si-H groups/chain, $M_n=10,300$ g/mol; ^c not determined.

Table S2. Grafting of diethylvinyl phosphonate onto PDMS-co-PHMS polymers catalyzed by $B(C_6F_5)_3$.^a

Run	PDMS	DEVPSi-H mol/mol	Conv. %	M_n SEC kg/mol	\bar{D}
entry 4	A	5.9	73	41	1.8
entry 5	A	2.6	92	32.5	2.1
entry 6	B	3.3	98	– ^c	– ^c
entry 7	C	3.3	72	– ^c	– ^c

^a Conditions : 1 eq Si-H; 0.17 eq $B(C_6F_5)_3$; m (Si-H) = m (Tol)=1 g; T = 85°C. ^b PDMSs A, B, C same as Table S1.

Table S3. Grafting of methyl vinyl sulfone onto PDMS-co-PHMS polymers catalyzed by $B(C_6F_5)_3$.^a

Run	PDMS	MVS/Si-H mol/mol	M_n SEC kg/mol	\bar{D}	characterizations
entry 8	A	1.2	53.5	1.5	TGA
entry 9	A	2.0	50.8	1.2	SEC, (E)SEM
entry 10	D	16.0	84.4	1.6	DSC
entry 11	E	5.0	– ^c	– ^c	Rheology

^a Conditions : 1 eq Si-H; 0.05 eq $B(C_6F_5)_3$; m (Si-H) = m (Tol)=1 g; T = 25°C. ^b PDMS A: telechelic hydride terminated poly(dimethylsiloxane), M_n =23,500 g/mol; PDMS D: 2.3 Si-H groups/chain, M_n =55,000 g/mol; PDMS E: 16 Si-H groups/chain, M_n =103,000 g/mol; ^c not determined.

Table S4. Grafting of allyl phenyl sulfone onto PDMS-co-PHMS polymers catalyzed by $B(C_6F_5)_3$.^a

Run	PDMS	APS/Si-H mol/mol	Characterizations
entry 11	A	2.0	¹ H NMR, TGA, DSC, SEM
entry 12 ^b	D	1.2	Rheology, DSC

^a Conditions : 1 eq Si-H; 0.05 eq $B(C_6F_5)_3$; m (Si-H) = m (Tol)=1 g; T = 25°C. ^b PDMSs A and D same as Tables S3; ^b 0.03 eq $B(C_6F_5)_3$, m (SiH) 2g.

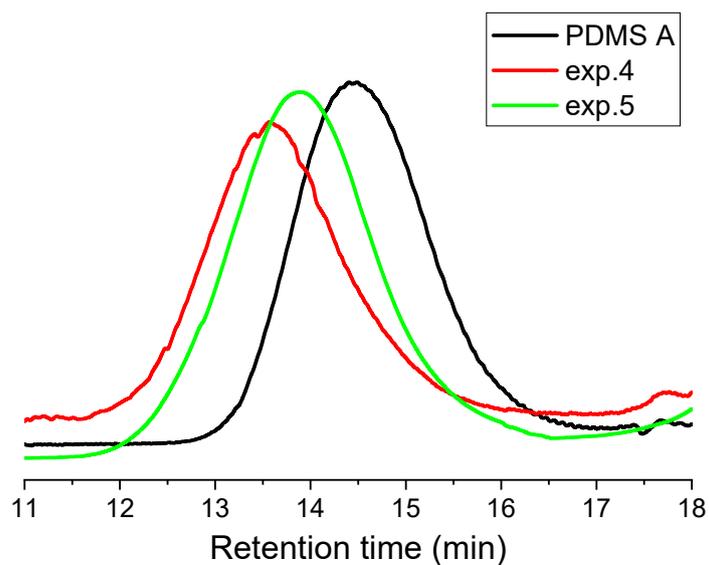


Figure S1. SEC curves of product of the reaction of telechelic PDMS A with DEVP.
For experimental details see Table S2.

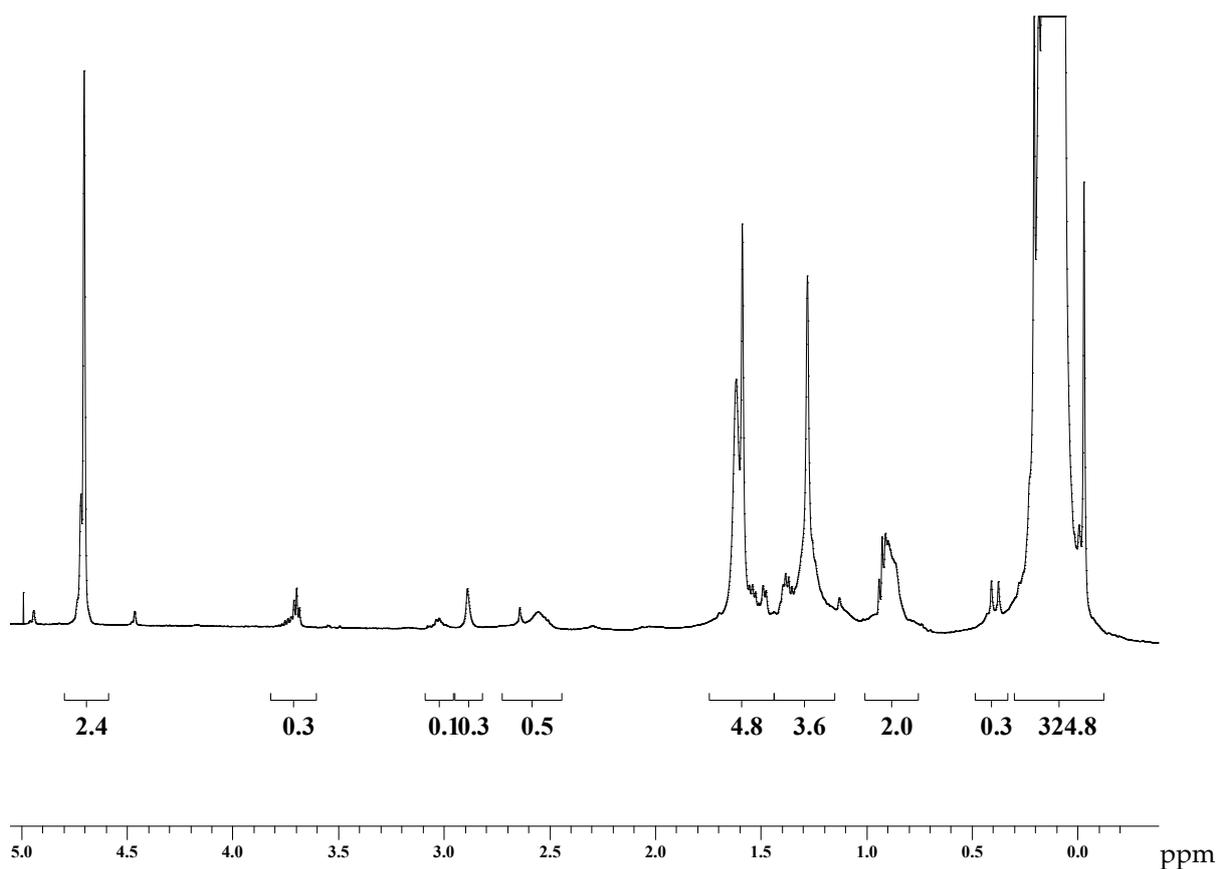


Figure S2. ¹H HR-MAS NMR spectrum of MVS-functionalized PDMS C (not shown in Table S3 since characterization were not possible, described in patent, see main text reference [37]). The peak at 4.5 ppm shows the content of SiH that did not react (here 50% conversion). Peaks at 2.9, 2.6, 1.5 and 0.4 ppm are representative of oligoMVS functionalization but their integration were not possible in such an ill-defined spectrum.

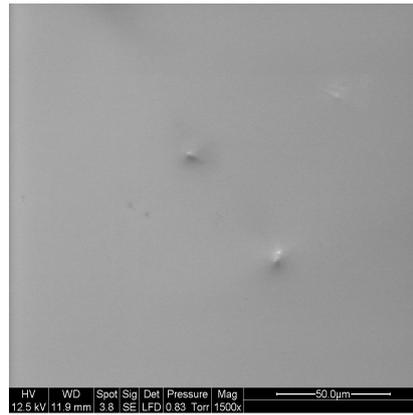


Figure S3. ESEM photo of MVS-functionalized block copolymer (Run 8, Table S3).

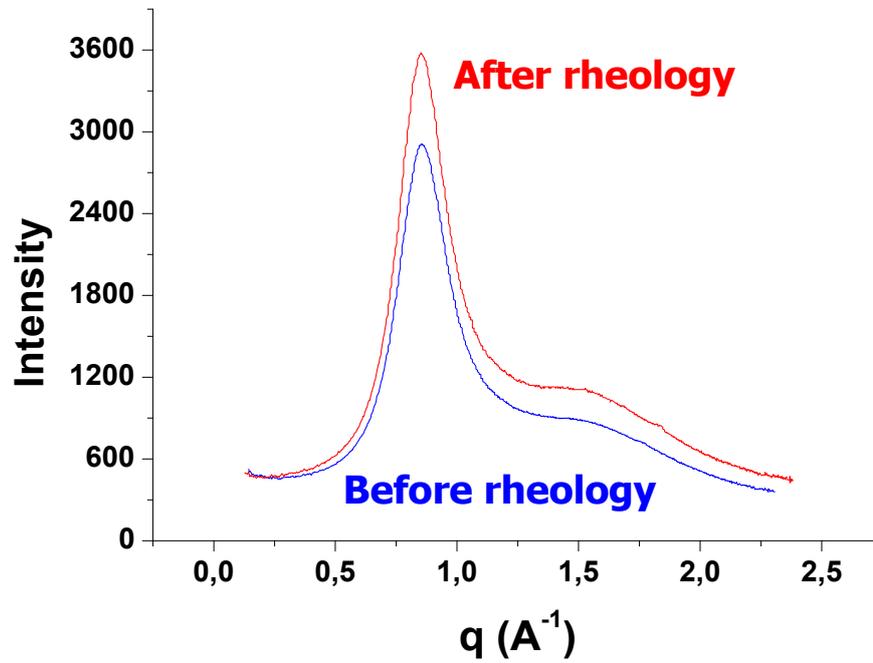


Figure S4: X-ray diffraction of the sulfonated PDMS (run 11, table S4) before and after rheology analysis.

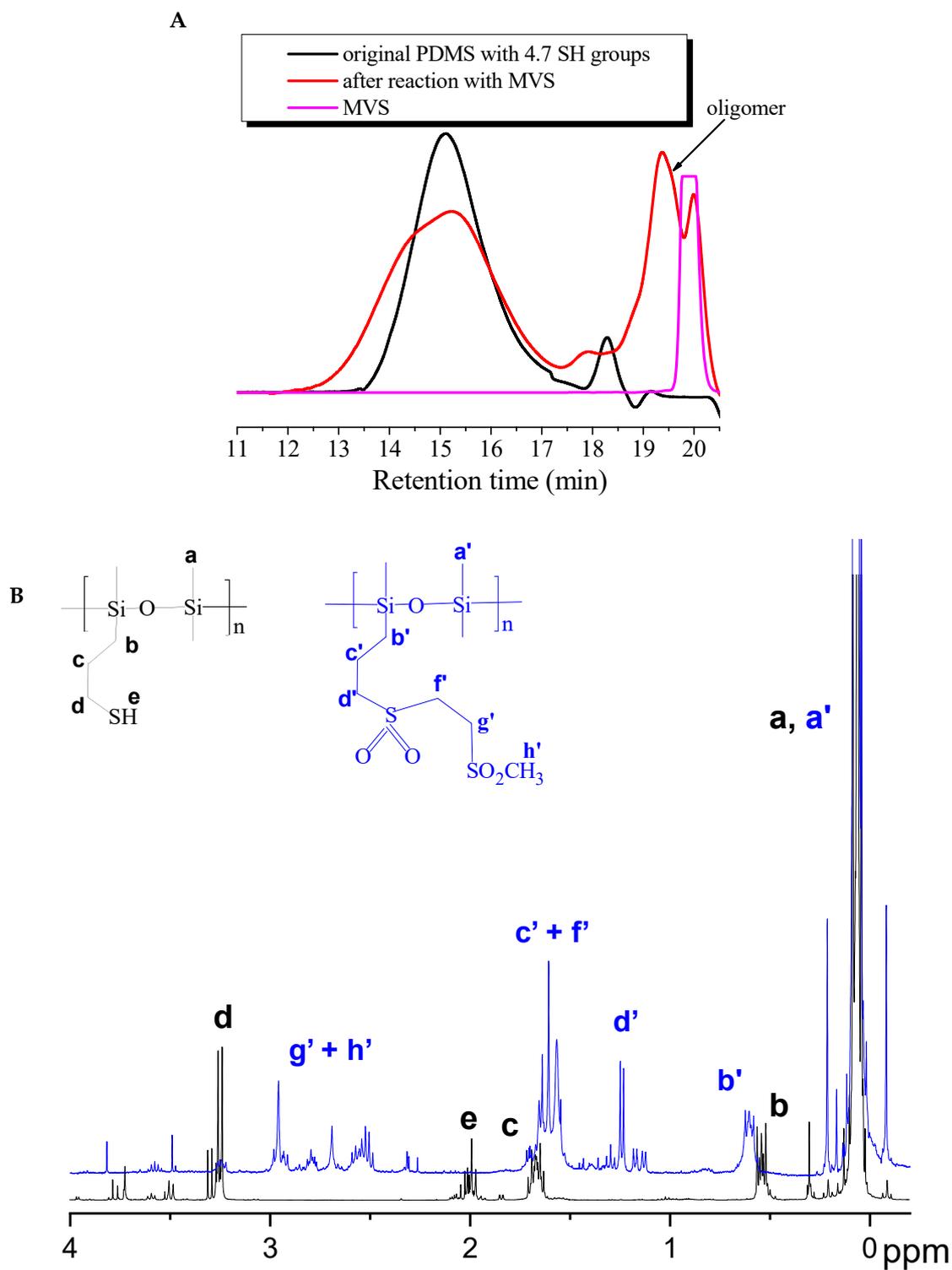


Figure S5. (A) SEC curves of product of the thiol-ene monoaddition of MVS on 4-6% mercaptopropylmethyl siloxane-dimethylsiloxane copolymer. (B) Full ^1H NMR spectra of pristine PDMS (black) and polysiloxane-g-bis-sulfone (blue). Peak of SH (e at 2 ppm) has disappeared whereas the integral of c peak quadruples. The d signal is shifted down to 1.3 ppm after sulfonation.