Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

One-pot syntheses of heterotelechelic α-vinyl,ω-methoxysilane polyethylenes and condensation into comb-like and star-like polymers with high chain end functionality.

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Alkoxysilyl-PE isolated after deactivation with TMOS (Si/Mg = 0.5, pre-diluted in toluene) of PE-Mg-PE chains obtained at 70°C by CCG using [(C5Me5)2NdCl2Li(OEt2)2]/BOMAG catalytic system.

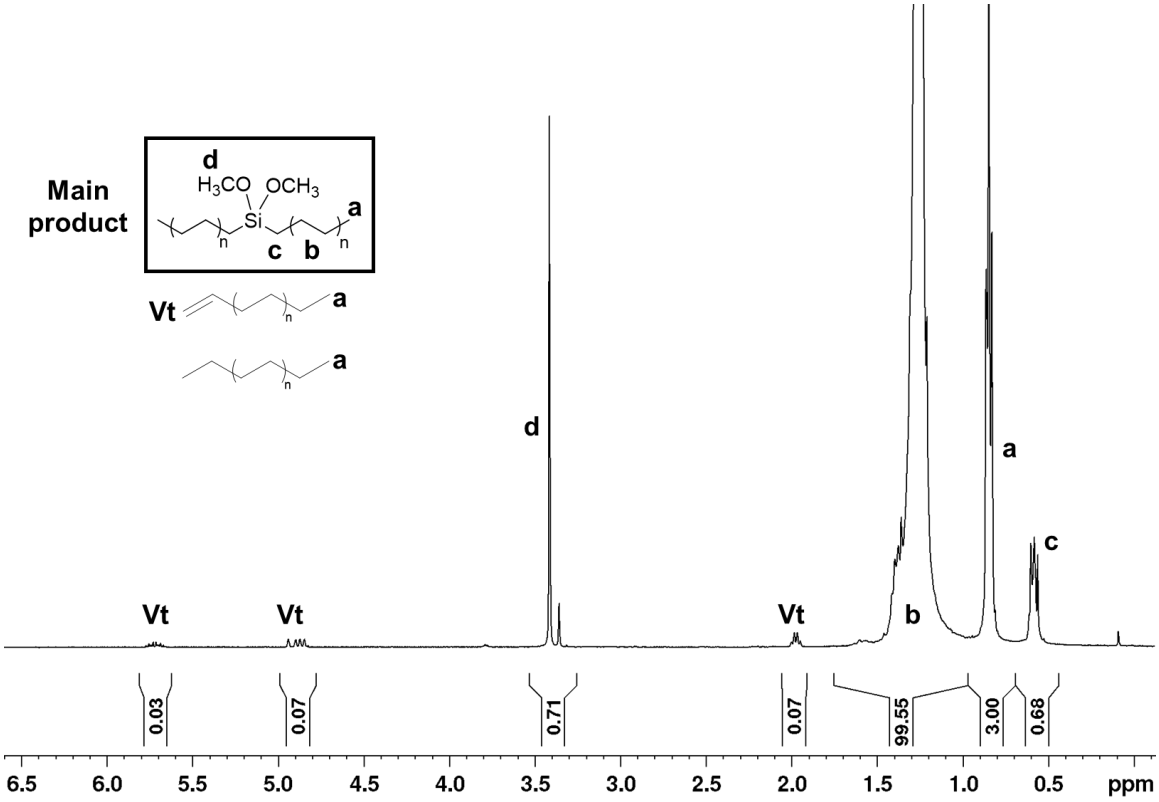


Figure S1. ^{1}H NMR spectrum of alkoxysilyl-PE isolated after deactivation with an amount of TMOS (Si/Mg = 0.5) of PE-Mg-PE chains obtained by CCG using $[(C_5Me_5)_2NdCl_2Li(OEt_2)_2]$/BOMAG catalytic system

^{1}H NMR (TCE/C_6D_6 2/1, 400 MHz, 363 K) δ ppm: 0.57 (c), 0.84 (a), 1.26 (b), 1.97 (Vt), 3.41 (d), 4.89 (Vt), 5.74 (Vt)

Determination of the number of PE chains per silicon atom:

Number of PE per silicon atom = $4*(I_{\text{-}CH_2\text{-}Si}/2) / ((I_{\text{-}CH_2\text{-}Si}/2) + (I_{\text{-}SiOCH_3}/3)) = 2.36$

Number of corresponding methoxysilane group = $4*(I_{\text{-}SiOCH_3}/3) / ((I_{\text{-}CH_2\text{-}Si}/2) + (I_{\text{-}SiOCH_3}/3)) = 1.64$

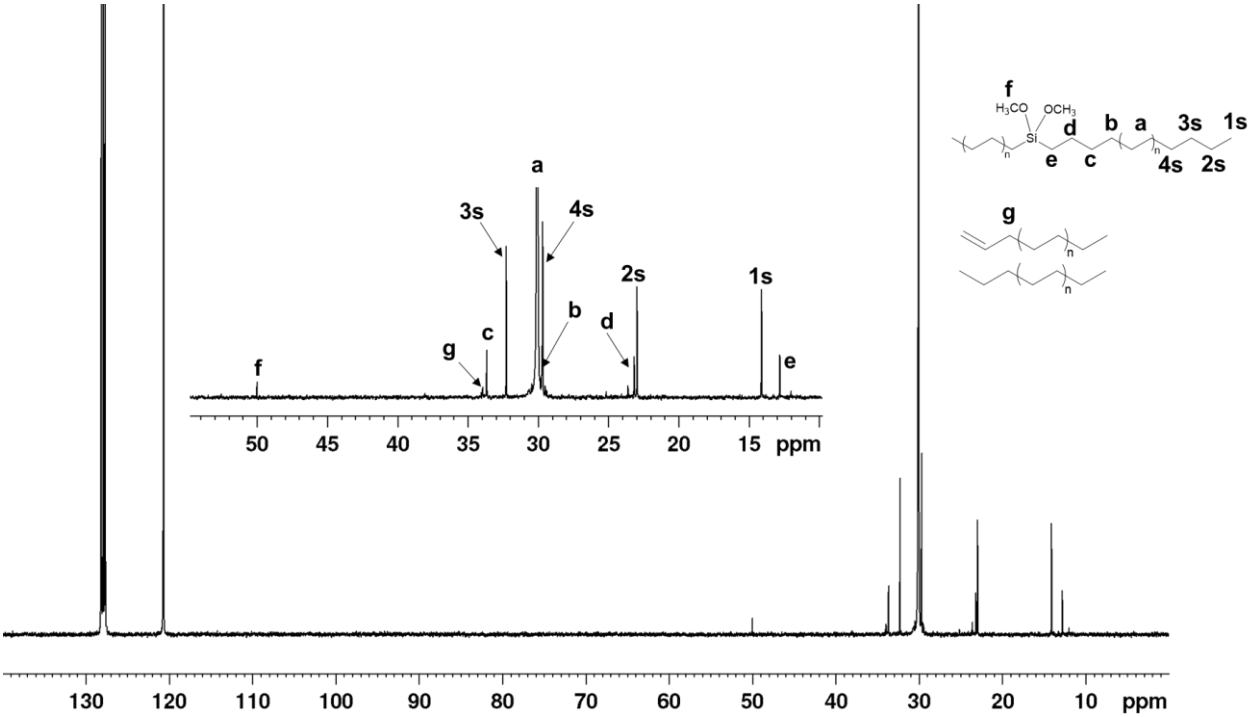


Figure S2. ^{13}C NMR spectrum alkoxysilyl-PE isolated after deactivation with TMOS (Si/Mg = 0.5) of PE-Mg-PE chains obtained by CCG using $[(C_5Me_5)_2NdCl_2Li(OEt_2)_2]$/BOMAG catalytic system

^{13}C NMR (TCE/C_6D_6 2/1, 100 MHz, 363 K) δ ppm: **12.78** (e), 14.08 (1s), 22.95 (2s), 23.15 (d), 29.66 (4s), 29.71 (b), 30.06 (a), 32.26 (3s), 33.65 (c), 50.01 (f)

***Alkoxysilyl-PE isolated after deactivation with an excess amount of functionalizing agent (Si/Mg = 10) of PE-Mg-PE chains obtained at 70°C by CCG using [$(C_5Me_5)_2NdCl_2Li(OEt_2)_2$]/*di(10-undecenyl)magnesium *catalytic system*.**

Table S1. Determination of the number of PE chains per silicon atom

	I_{-CH_2-Si}	I_{-SiOCH_3}	Number of PE per silicon atom	Number of corresponding methoxysilane group
Vin-PE-DMMS	1.63	4.54	1.05	1.95
Vin-PE-DMVS	1.81	4.67	1.10	1.90
Vin-PE-TMS	1.5	6.51	1.03	2.97

Number of PE per silicon atom = $x*(I_{-CH_2-Si}/2) / ((I_{-CH_2-Si}/2) + (I_{-SiOCH_3}/3))$

Number of corresponding methoxysilane group = $x*(I_{-SiOCH_3}/3) / ((I_{-CH_2-Si}/ 2) + (I_{-SiOCH_3}/3))$

x=3 for Vin-PE-DMMS, Vin-PE-DMVS and x=4 for Vin-PE-TMS

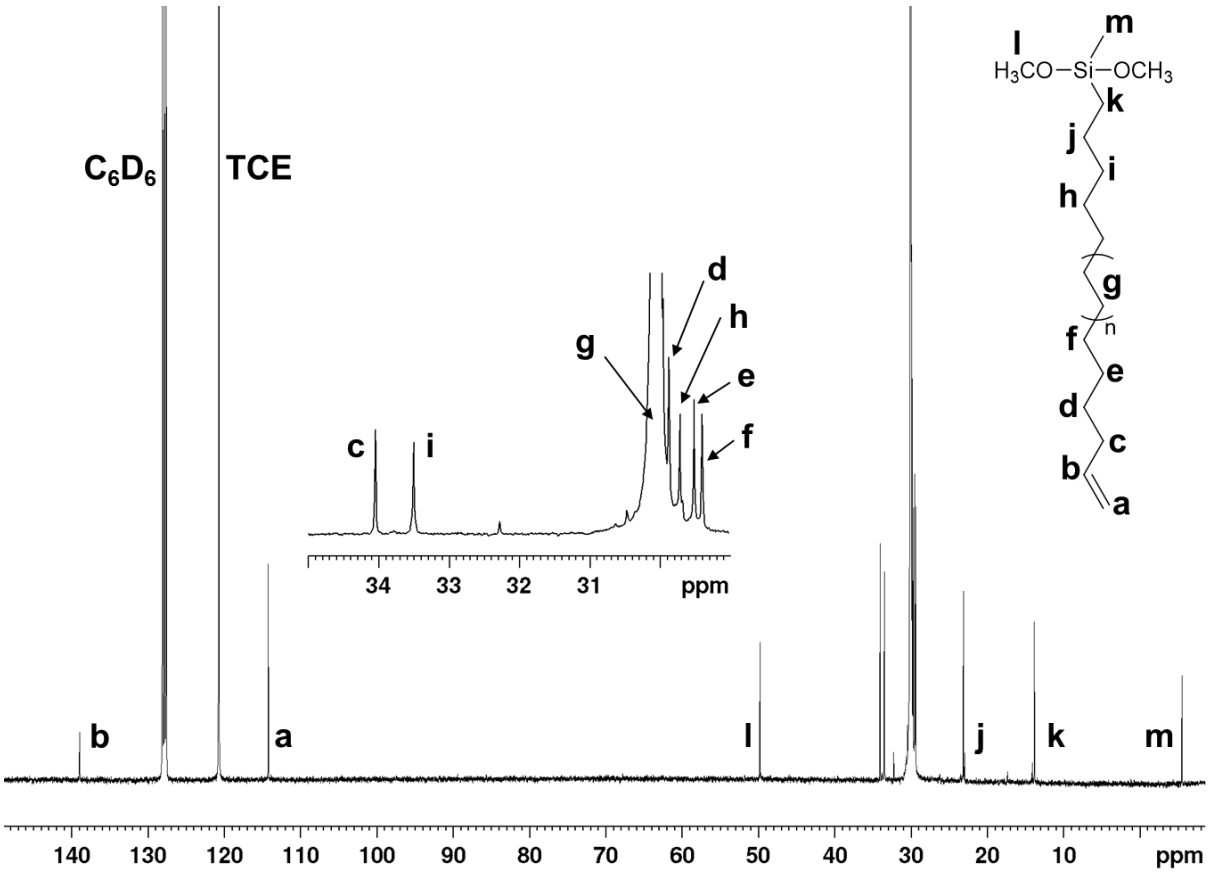


Figure S3. ^{13}C NMR spectrum of Vin-PE-DMMS isolated after deactivation with an excess amount of TMMS (diluted in dried toluene, Si/Mg = 10) of PE-Mg-PE chains obtained at 70°C by CCG using $[(C_5Me_5)_2NdCl_2Li(OEt_2)_2]$/di(10-undecenyl)magnesium catalytic system

^{13}C NMR (TCE/C_6D_6 2/1, 100 MHz, 363 K) δ ppm: -5.51 (m), 13.82 (k), 23.12 (j), 29.38 (f), 29.50 (e), 29.70 (h), 29.86 (d), 30.06 (g), 33.49 (i), 34.04 (c), 49.80 (l), 114.25 (a), 138.96 (b)

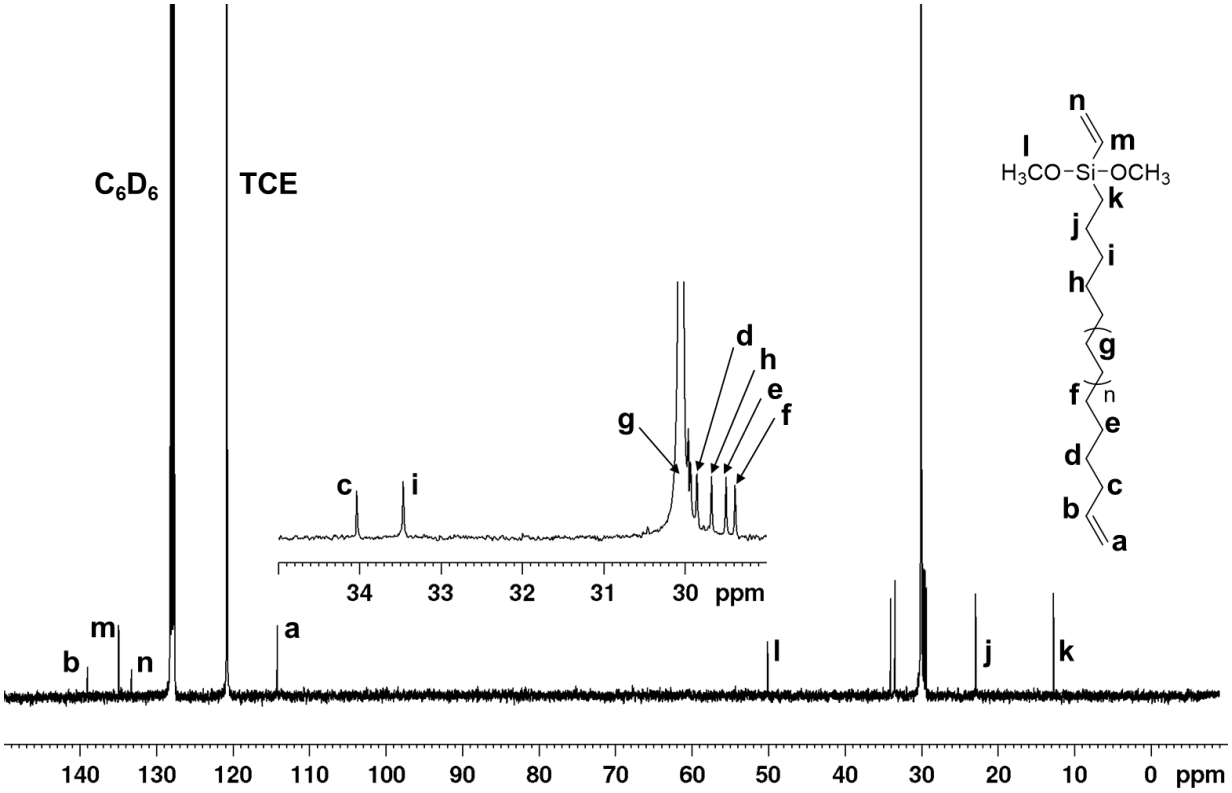


Figure S4. ^{13}C NMR spectrum of Vin-PE-DMVS isolated after deactivation with an excess amount of TMVS (diluted in dried toluene, Si/Mg = 10) of PE-Mg-PE chains obtained at 70°C by CCG using $[(C_5Me_5)_2NdCl_2Li(OEt_2)_2]$/di(10-undecenyl)magnesium catalytic system

^{13}C NMR (TCE/C_6D_6 2/1, 100 MHz, 363 K) δ ppm: 12.75 (k), 22.92 (j), 29.38 (f), 29.49 (e), 29.67 (h), 29.85 (d), 30.06 (g), 33.47 (i), 34.04 (c), 50.15 (l), 114.25 (a), 133.23 (n), 134.89 (m), 138.98 (b)

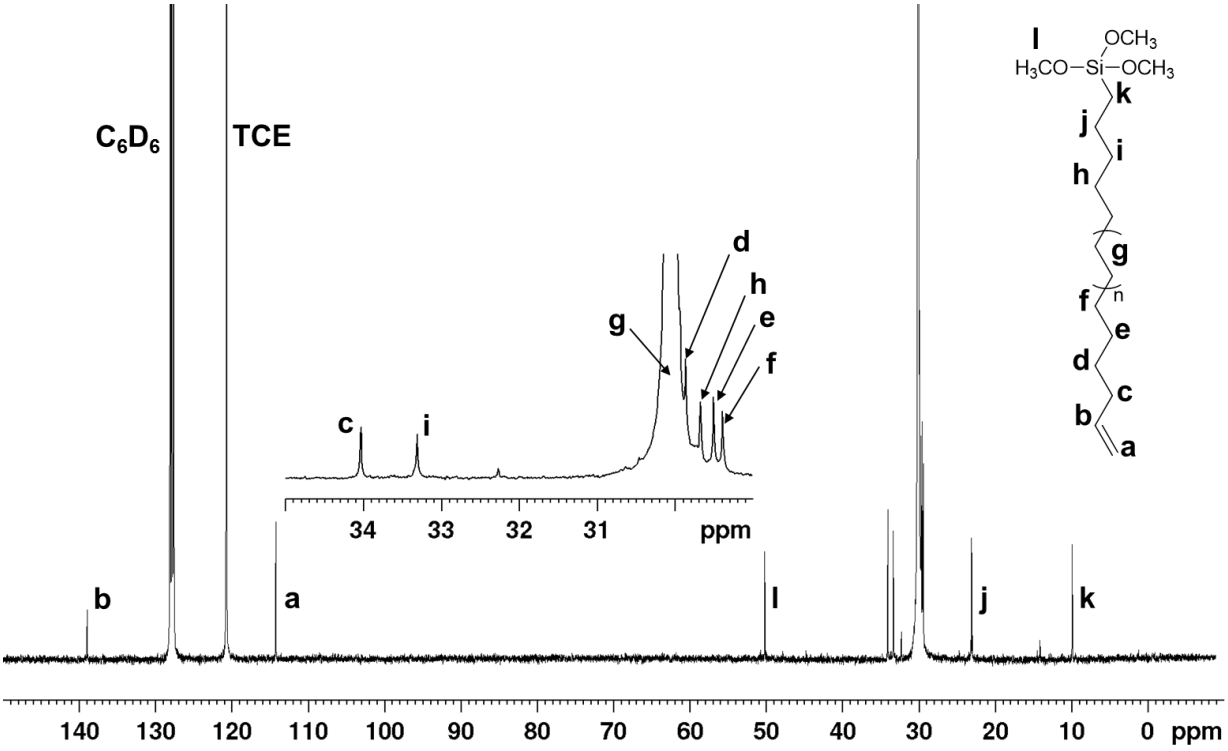


Figure S5. ^{13}C NMR spectrum of Vin-PE-TMS isolated after deactivation with an excess amount of TMOS (Si/Mg = 10) of PE-Mg-PE chains obtained by CCG using $[(C_5Me_5)_2NdCl_2Li(OEt_2)_2]$/di(10-undecenyl)magnesium catalytic system

^{13}C NMR (TCE/C_6D_6 2/1, 100 MHz, 363 K) δ ppm: 9.86 (k), 23.04 (j), 29.38 (f), 29.49 (e), 29.66 (h), 29.85 (d), 30.06 (g), 33.31 (i), 34.03 (c), 50.15 (l), 114.25 (a), 138.98 (b)

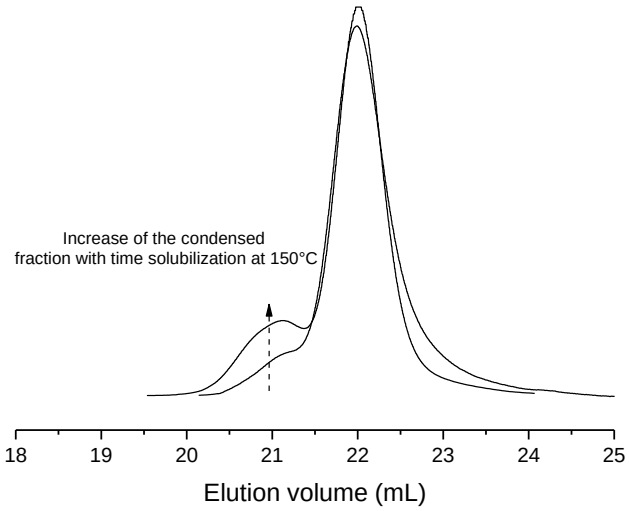


Figure S6. HT-SEC (150°C in TCB) of Vin-PE-DMMS. The two samples have been respectively left for solubilization during 15 min and 5h in TCB at 150°C before HT SEC analysis.

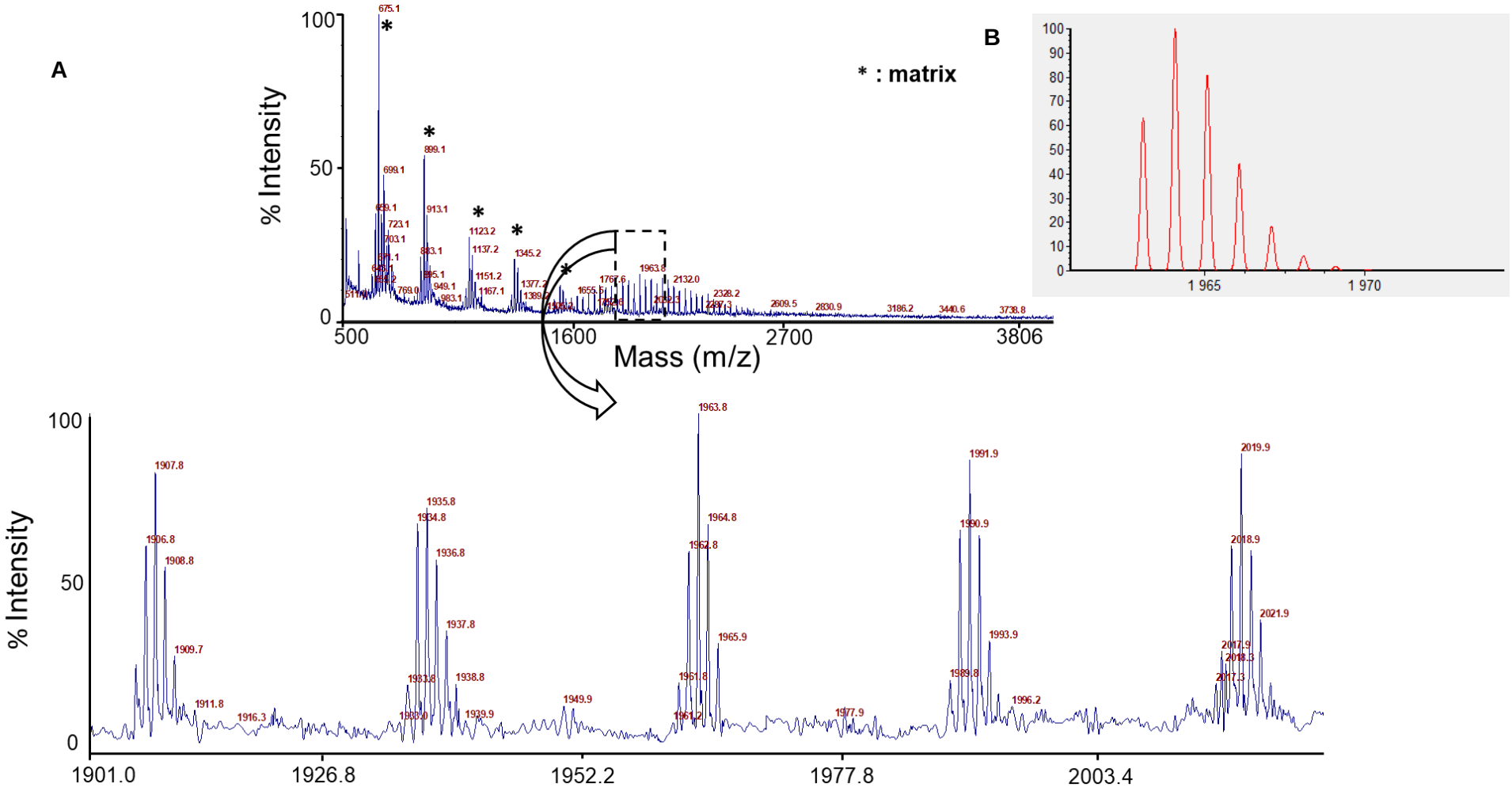


Figure S7. A) MALDI-TOF MS analysis of Vin-PE-DMMS in the reflectron mode using dithranol as matrix and B) simulation of the isotopic distribution using ISOPRO software.

m/z 1962.8 = 105.04 + (**n** x 28.03) + 41.04 +23, **n** = 64, formula of the polymer: $C_{128}H_{256}$ + $C_6H_{14}O_2SiNa$
Isopro simulation: C_{134} H_{270} O_2 Na_1 Si_1

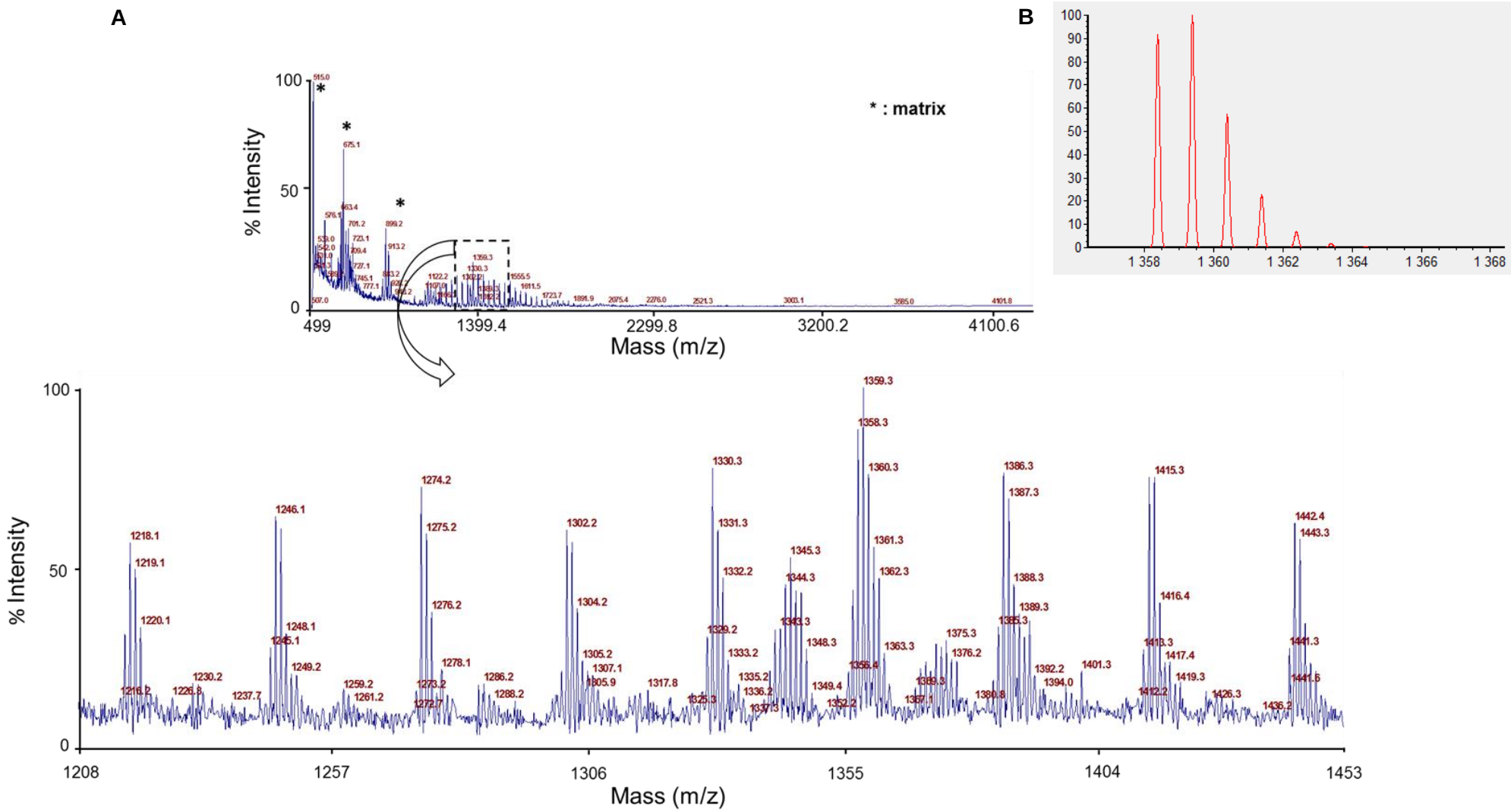
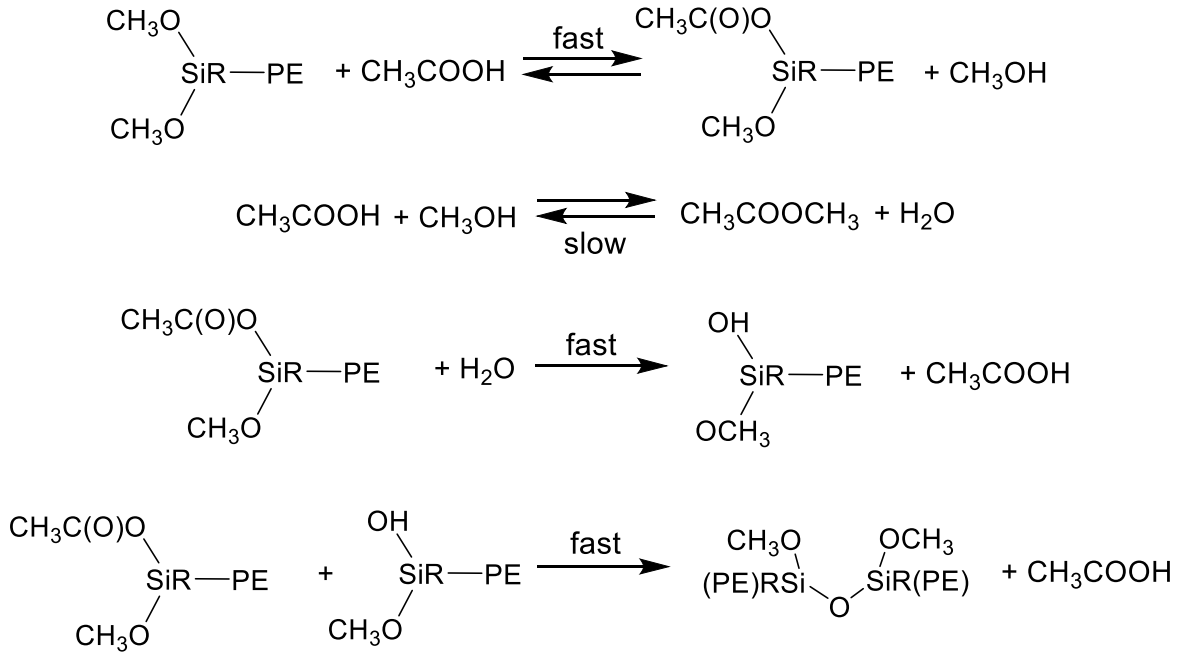


Figure S8. A) MALDI-TOF MS analysis of Vin-PE-DMVS in the reflectron mode using dithranol as matrix and B) simulation of the isotopic distribution using ISOPRO software

m/z 1358.3 = 117.04 + (**n** x 28.03) + 41.04 +23, **n** = 42, formula of the polymer: $C_{84}H_{168}$ + $C_7H_{14}O_2SiNa$

Isopro simulation: C_{91} H_{182} O_2 Na_1 Si_1



Scheme S1. Mechanism involved in the hydrolysis-condensation of alkoxysilyl-PE[1]

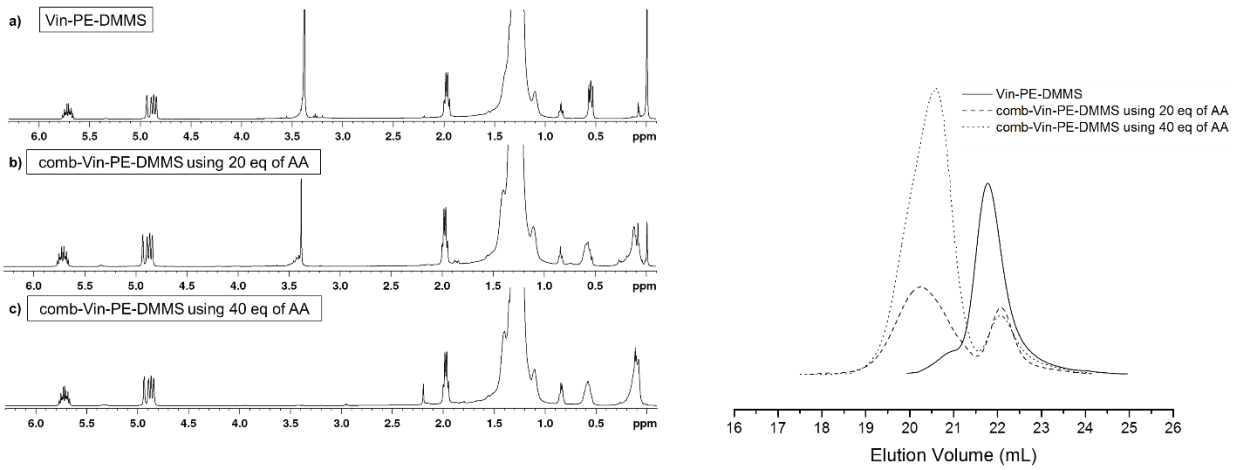


Figure S9. ^{1}H NMR spectra of a) Vin-PE-DMMS, b) comb-Vin-PE-DMMS (20 eq) and c) comb-Vin-PE-DMMS (40 eq)

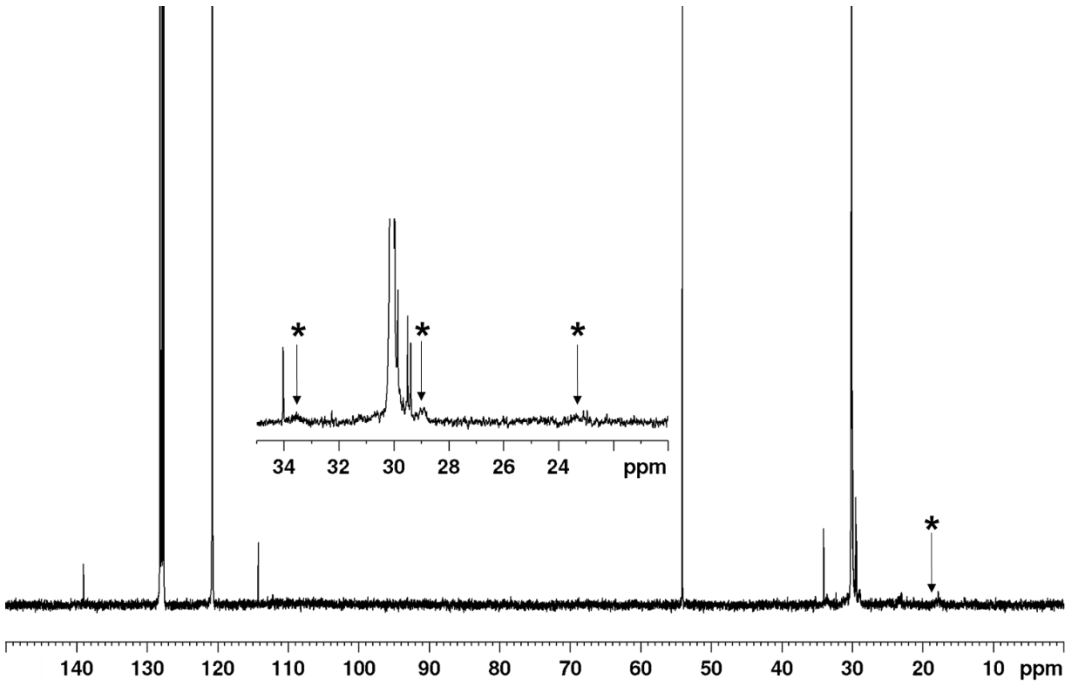


Figure S10. ^{13}C NMR spectrum of comb-Vin-PE-DMMS, * corresponds to carbons adjacent to the silicon atom

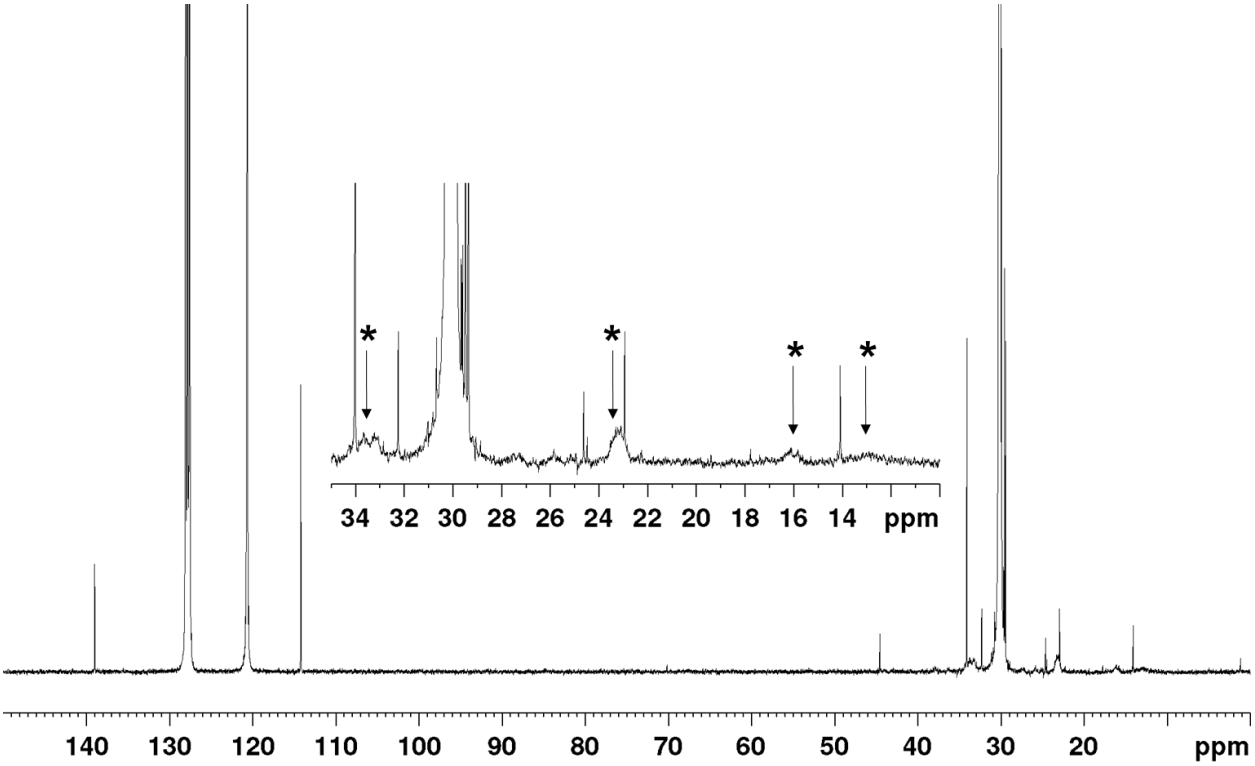


Figure S11. ^{13}C NMR spectrum of star-Vin-PE-TMS, * corresponds to carbons adjacent to the silicon atom

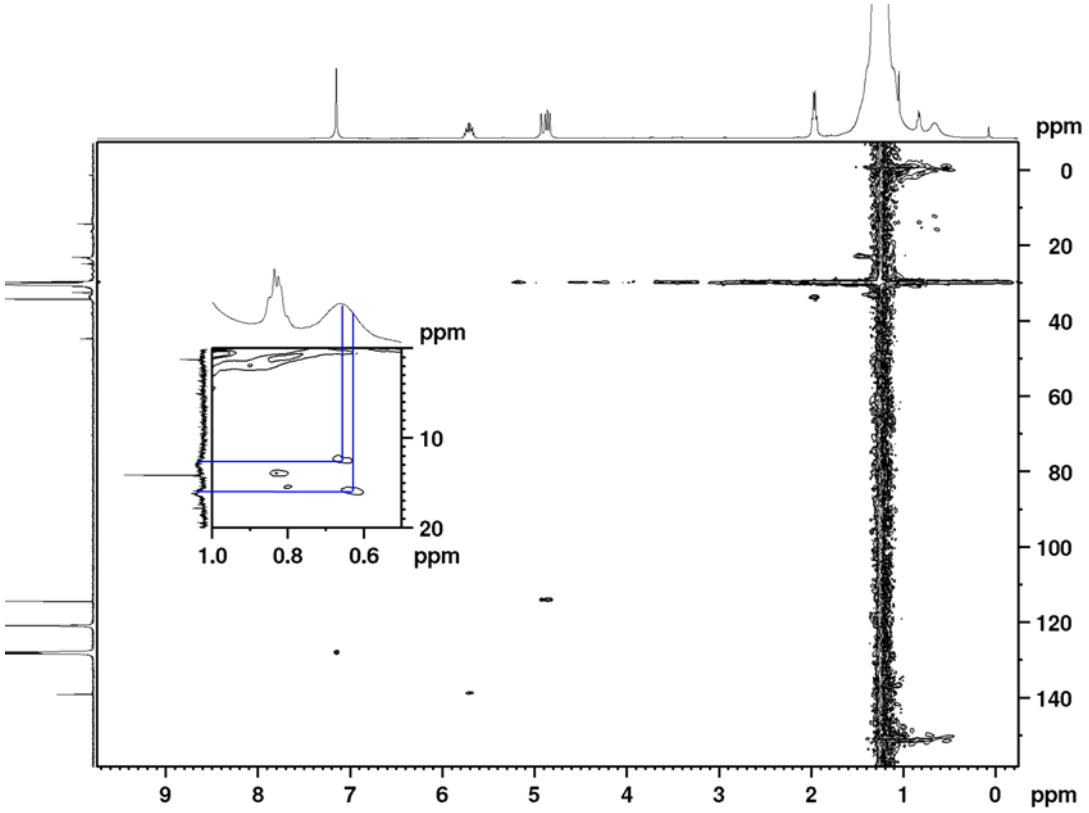


Figure S12. ^{1}H-^{13}C HSQC of star-Vin-PE-TMS

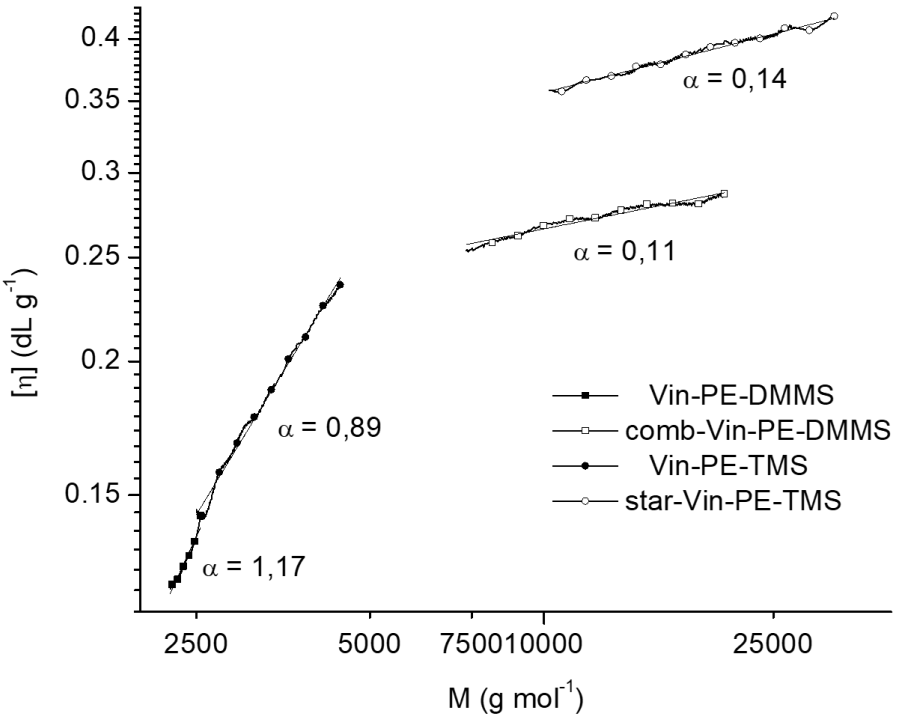


Figure S13. Mark-Houwink plots of Vin-PE-DMMS (filled squares), comb-Vin-PE-DMMS (open squares), Vin-PE-TMS (filled circles) and star-Vin-PE-TMS (open circles) obtained using the Mark-Houwink relation: $log[\eta] = \log(k) + \alpha\, logM$

Reference

1. E V. Egorova, NG. Vasilenko, N V. Demchenko, EA Tatarinova, AM Muzafarov. *Dokl. Chem.*, 2009, **424**, 15–18.