

Electronic Supplementary Information
for

**Making Accessible Soluble Silicon-Containing
Polynorbornenes: Hydrosilylation of Vinyl-Addition Poly(5-
vinyl-2-norbornene)**

Alyona I. Wozniak,^a Evgeniya V. Bermesheva,^{a,b} Ilya L. Borisov,^a Sergey
A. Rzhavskiy,^a Andrey A. Tyutyunov,^c Sergey O. Ilyin,^a Maxim A.
Topchiy,^a Andrey F. Asachenko,^a and Maxim V. Bermeshev^{*,a}

Fax: +7(495)633-85-20
Phone: +7(495) 647-59-27*379
E-mail address: bmv@ips.ac.ru

Table of contents

Experimental section.....	2
Physico-Chemical Characterization.....	2
Film Preparation	2
Measurements of gas-transport properties	3
NMR spectra of the modified polymers	4
NMR and Mass spectra of the hydrosilylated products of VNBA	9
GPC curves of the modified polymers.....	15
Gas permeation study for the modified vinyl-addition polynorbornenes	16
References.....	17

Experimental section

Physico-Chemical Characterization

NMR spectra were recorded on spectrometers Bruker Ascend 400 at 400.1 MHz (^1H) and 100.6 MHz (^{13}C) and Bruker MSL-300 at 300 MHz (^1H). Chemical shifts (δ) are reported in parts per million (ppm) relative to the reference (residual CHCl_3 signal) for ^1H and ^{13}C NMR spectra. For ^{29}Si NMR spectra the proton frequency of the solvent used as reference. Each sample was dissolved in CDCl_3 up to a concentration of 10%.

Gel-permeation chromatography (GPC) analysis of the polymers was performed on a Waters system with a differential refractometer (Chromatopack Microgel-5; eluent, chloroform; flow rate, 1 ml/min). The molecular weights and dispersity were calculated by a standard procedure relative to monodispersed polystyrene standards.

Calorimetric measurements were conducted using a Mettler TA-4000 differential scanning calorimeter (Giesen, Germany) at a heating rate of $20^\circ\text{C}/\text{min}$ under argon. TGA measurements were carried out on "TGA/DSC 1" (Mettler Toledo) in argon and air at the heating rate of $10^\circ\text{C}/\text{min}$ from 30 to 1000°C .

The temperature dependences of the loss tangent ($\tan\delta$) were measured by the DMA method on a rotational rheometer Discovery HR-2 (TA Instruments, USA) in the small-amplitude oscillatory tensile mode of polymer films at a frequency of 1 Hz and a temperature rise rate of $5^\circ\text{C}/\text{min}$.

Wide-angle X-ray diffraction (WAXD) data were obtained using a two-coordinate AXS detector (Bruker, Bremen, Germany) and $\text{Cu K}\alpha$ emission (wavelength of 0.154 nm).

The density of polymer films was determined by hydrostatic weighing according to the following procedure. A film was weighed on an analytical balance (m_{dry}). Then the thin copper wire was hung on a beam over the balance, and the film was fixed on the lower end of the wire, immersed in the beaker with methanol placed on the balance, and weighed (m_1). After that, the film was withdrawn, and the free wire end immersed in methanol was weighed (m_2). The density of film samples was calculated by the formula: $d = d_S m_{\text{dry}} / (m_{\text{dry}} - (m_1 - m_2))$, where $d_S = 0.791$ g/ml is the density of methanol.

Film Preparation

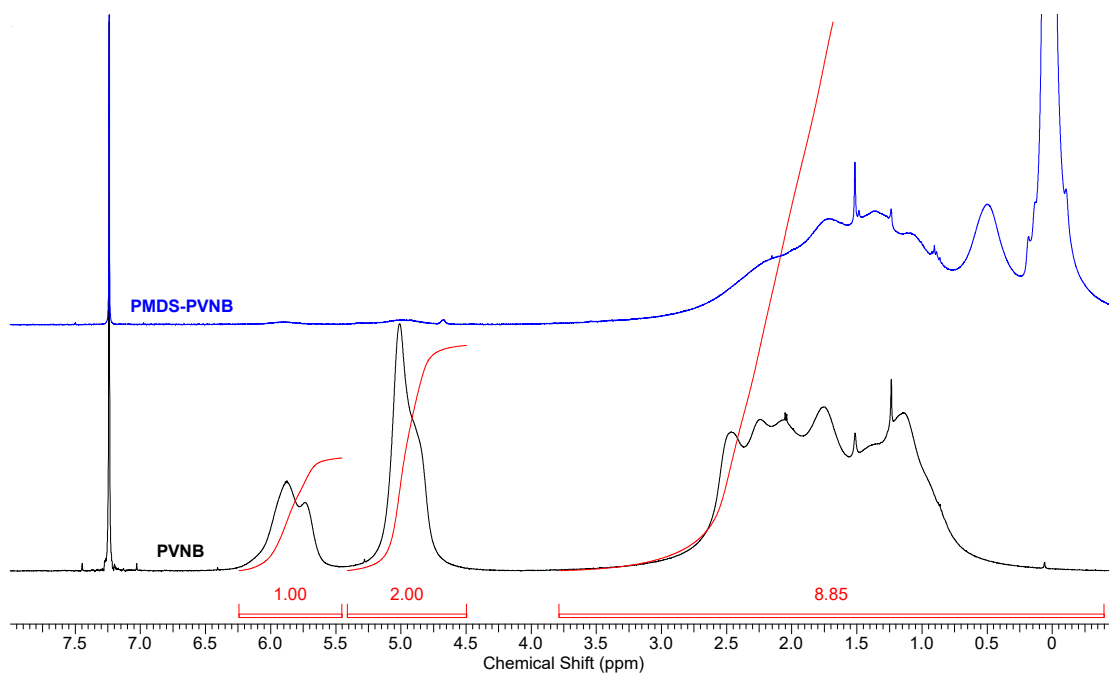
The polymer films for gas permeation and DMA study were prepared by casting from a 5 wt.% toluene solution of the polymer. The solution was poured into a steel cylinder with a diameter of 7 cm and a stretched cellophane bottom. The solvent was allowed to evaporate slowly at room temperature to yield the desired polymer films. After the formation of the films, the cellophane was detached, and the films were dried under vacuum at room temperature to a constant weight.

Thermal treatment was not applied. The thickness of the films formed was in the range of 90–110 μm . The properties of the obtained membranes were measured immediately after vacuumization. The time of a sample investigation was 2–5 days.

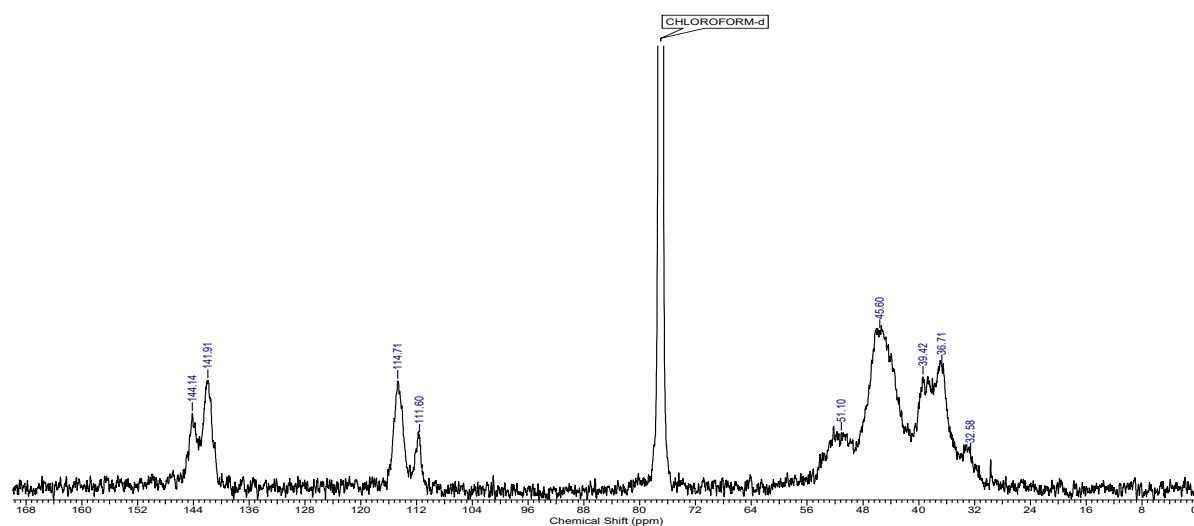
Measurements of gas-transport properties

Pure gas permeability and diffusion coefficients of gases were determined according to the Daynes–Barrer technique using precise unit “Helmholtz-Zentrum Geesthacht” mounted with a pressure sensor Baratron (MKS Instruments, accuracy 10^{-7} bar) at 30°C. The permeability coefficient is given in Barrer. The sorption coefficient was calculated as the ratio of the permeability coefficient to the diffusion coefficient.

NMR spectra of the modified polymers



(a)



(b)

Fig. S1 (a) ^1H NMR spectra of PVNB (bottom) and PMDS-PVNB (top) in CDCl_3 ; (b) ^{13}C NMR spectrum of PVNB (CDCl_3).

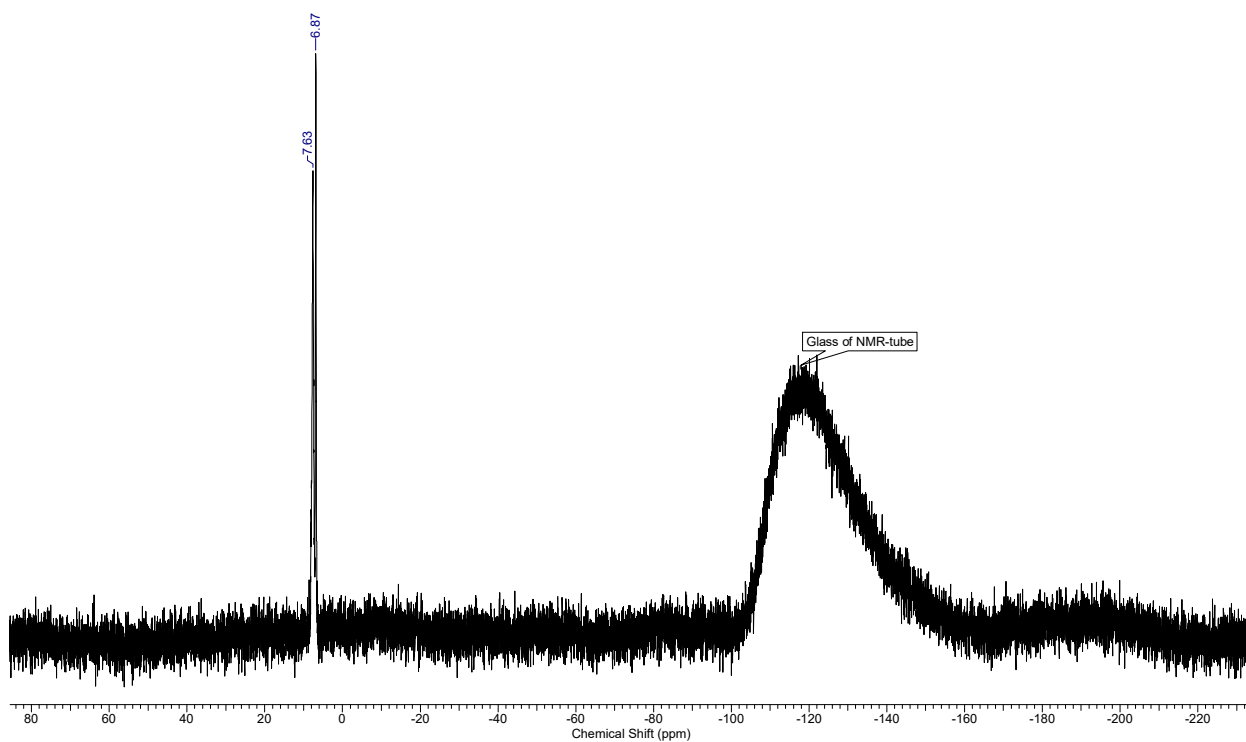
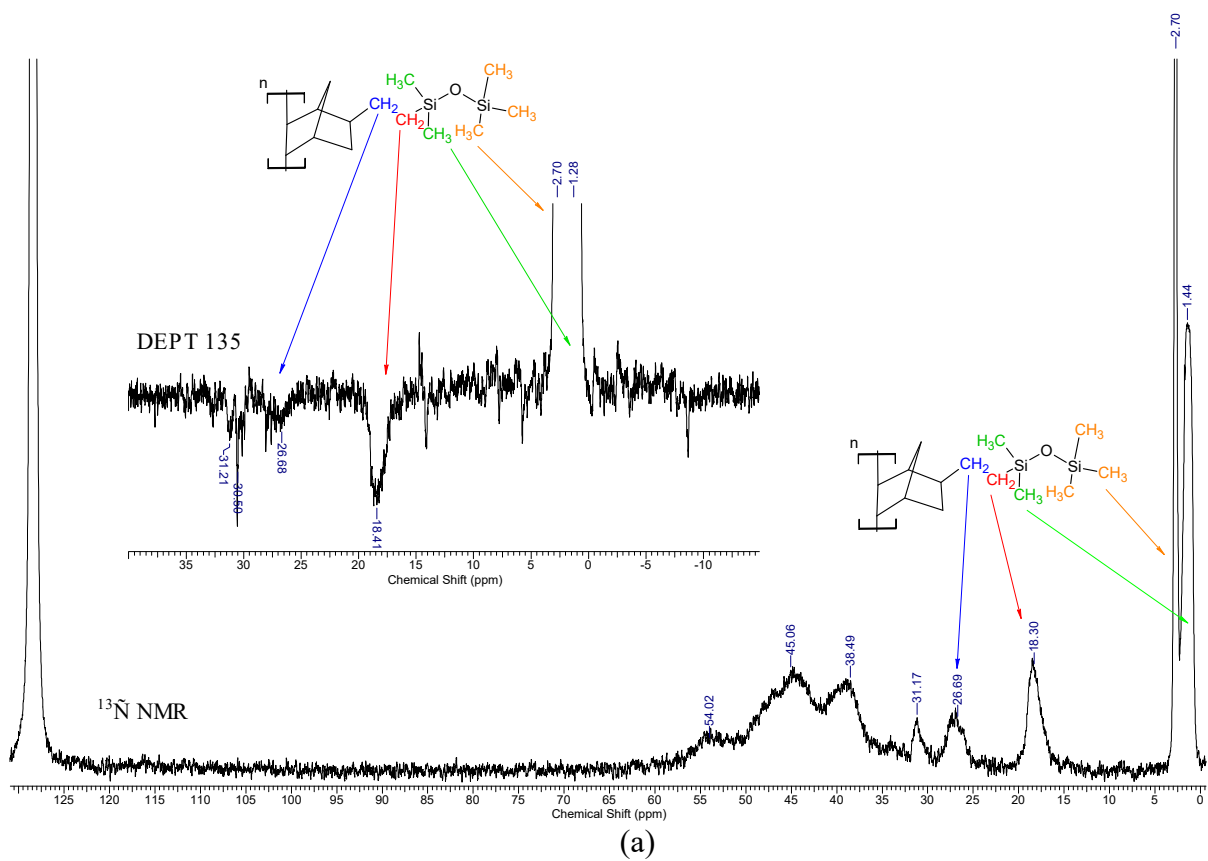


Fig. S2 (a) ¹³C and DEPT-135 NMR spectra of PMDS-PVNB in CDCl₃; (b) ²⁹Si NMR spectrum of PMDS-PVNB (CDCl₃).

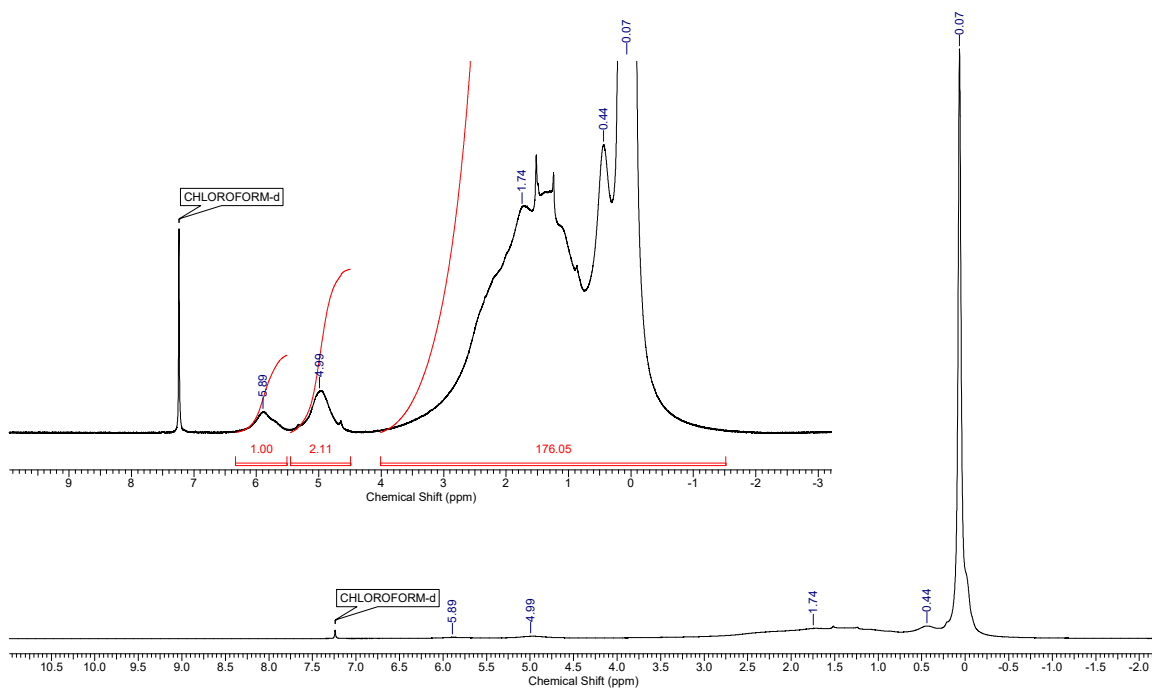


Fig. S3 ^1H NMR spectrum of HMTS-PVNB (CDCl_3).

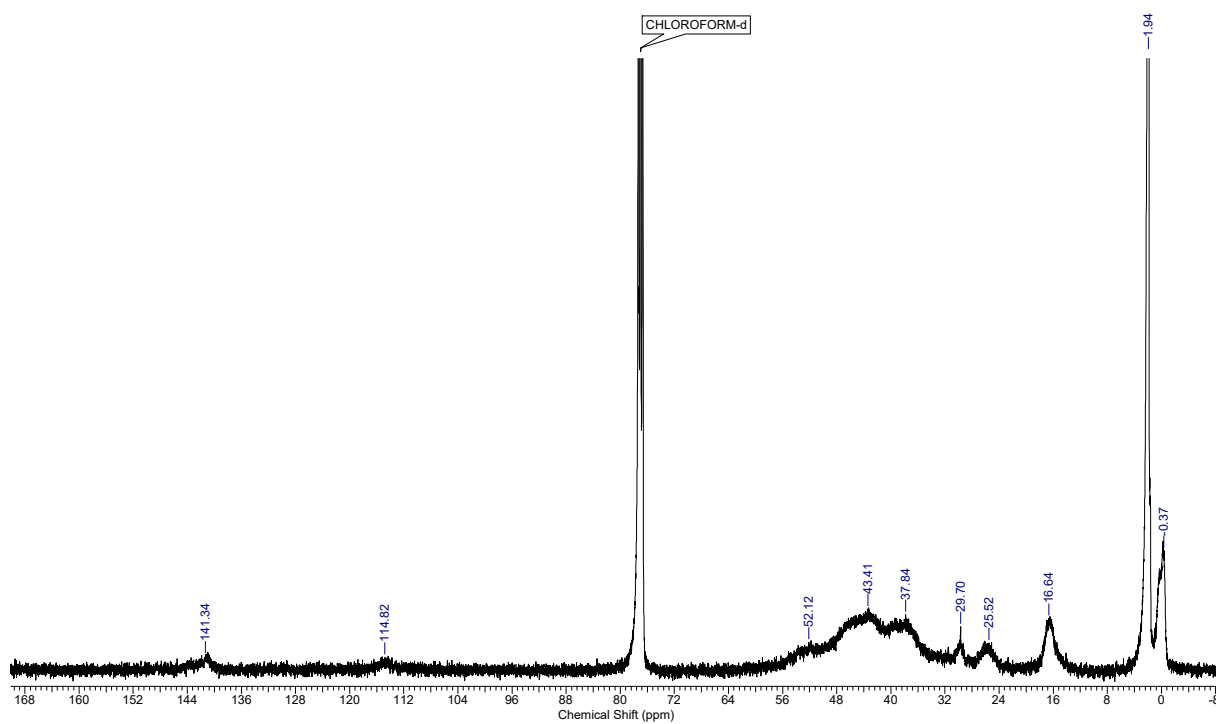


Fig. S4 ^{13}C NMR spectrum of HMTS-PVNB (CDCl_3).

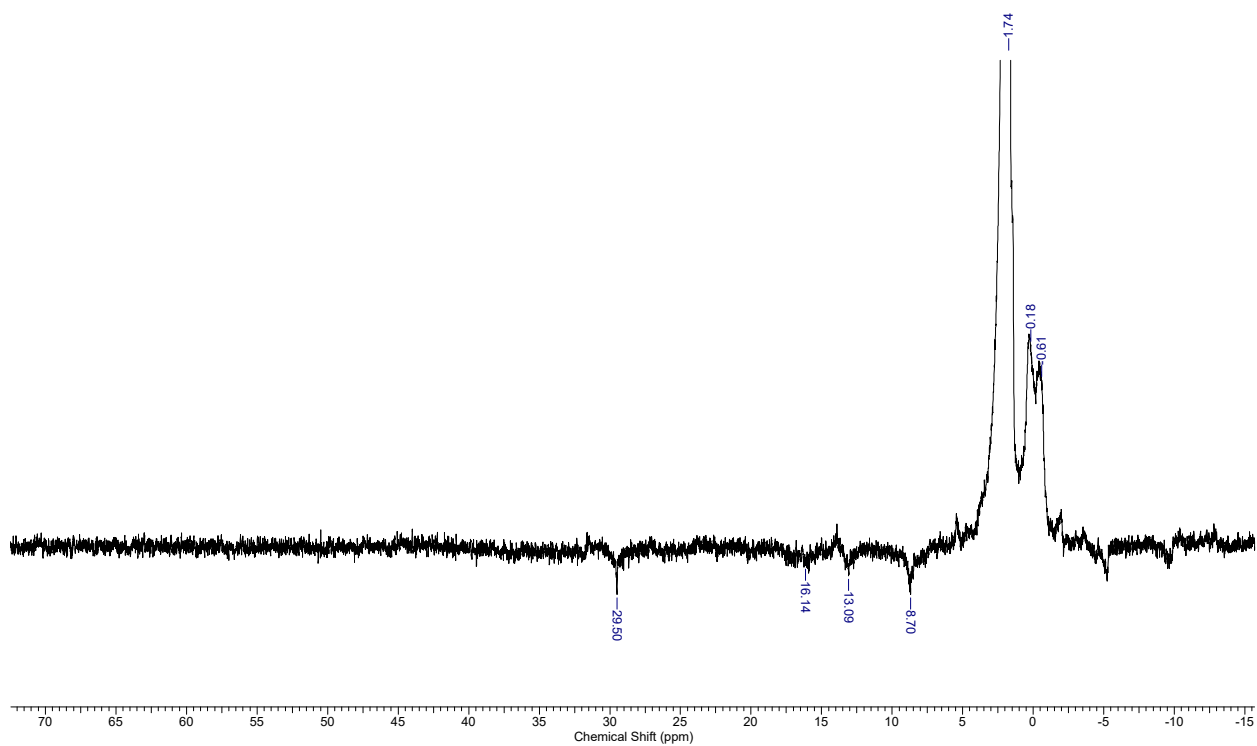


Fig. S5 DEPT-135 NMR spectrum of HMTS-PVNB (CDCl_3).

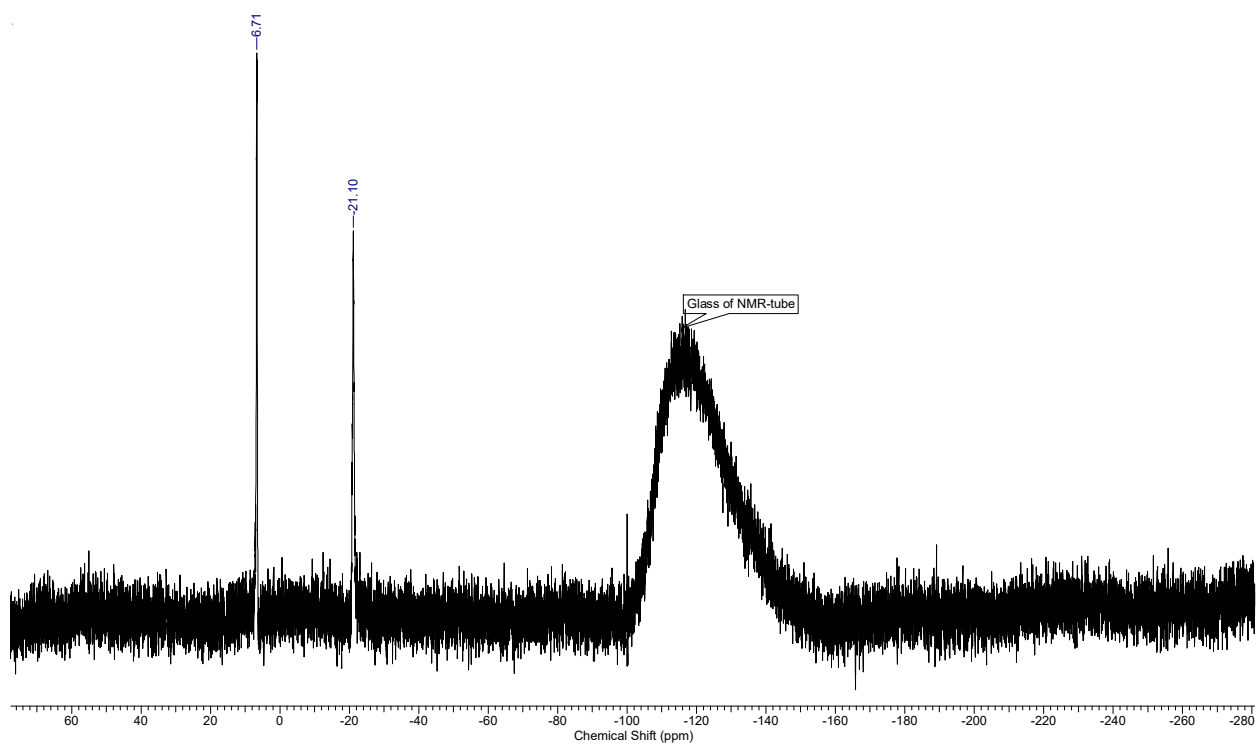


Fig. S6 ^{29}Si NMR spectrum of HMTS-PVNB (CDCl_3).

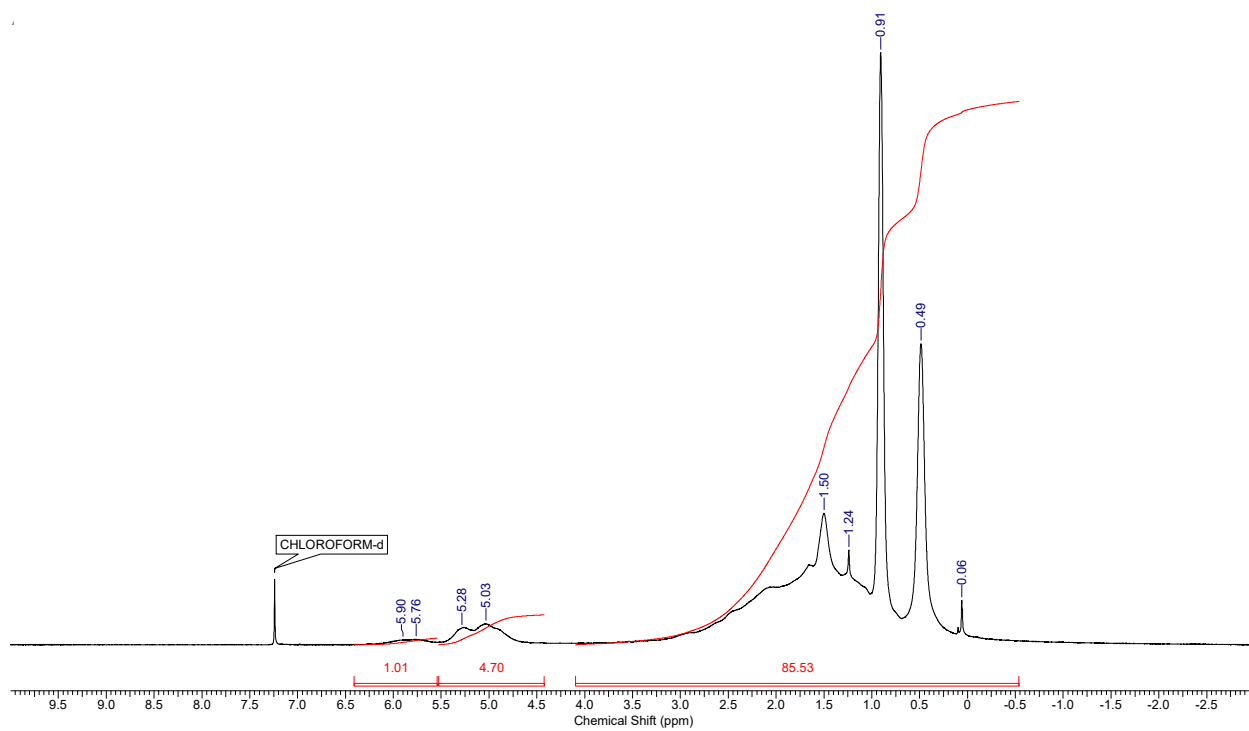


Fig. S7 ¹H NMR spectrum of Et₃Si-PVNB (CDCl₃).

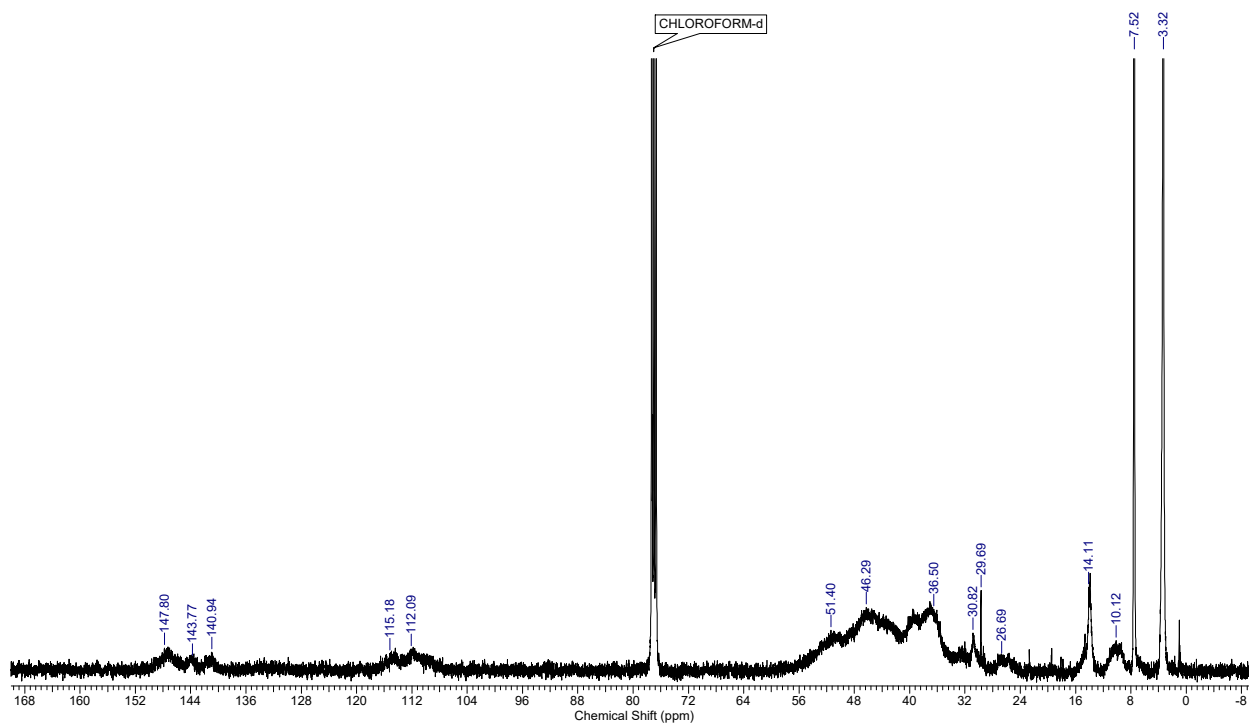


Fig. S8 ¹³C NMR spectrum of Et₃Si-PVNB (CDCl₃).

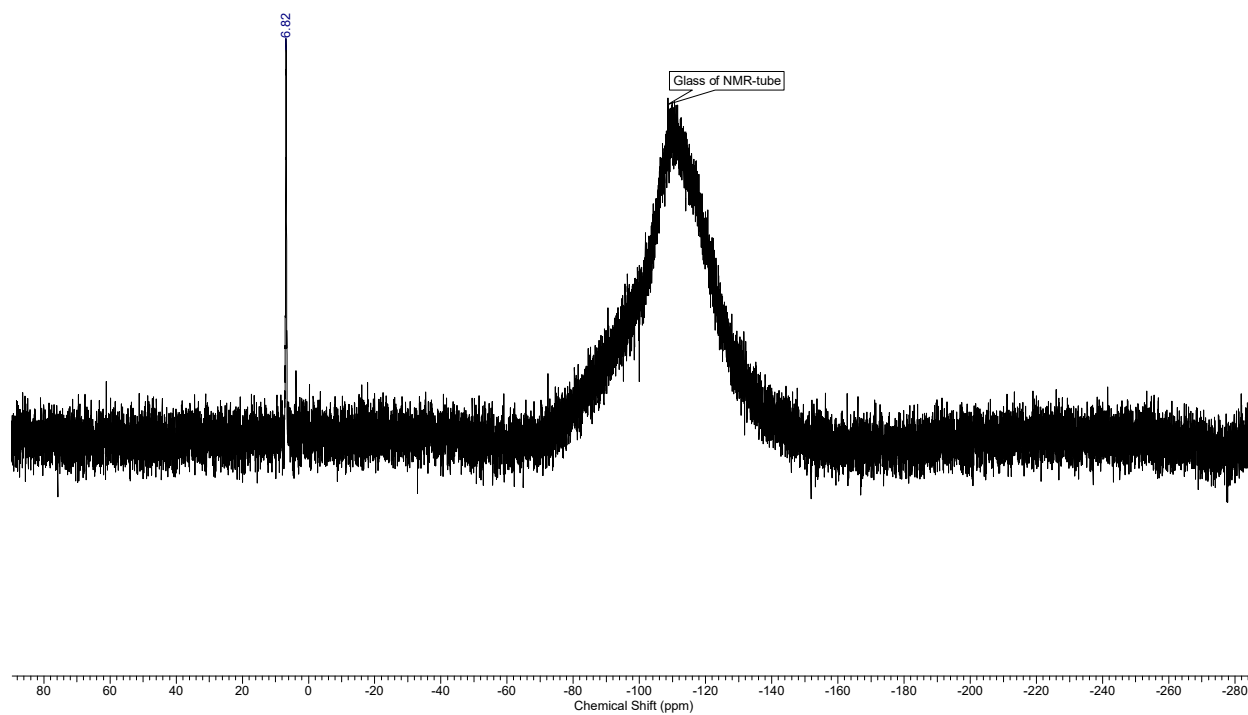


Fig. S9 ^{29}Si NMR spectrum of $\text{Et}_3\text{Si-PVNB}$ (CDCl_3).

NMR and Mass spectra of the hydrosilylated products of VNBA

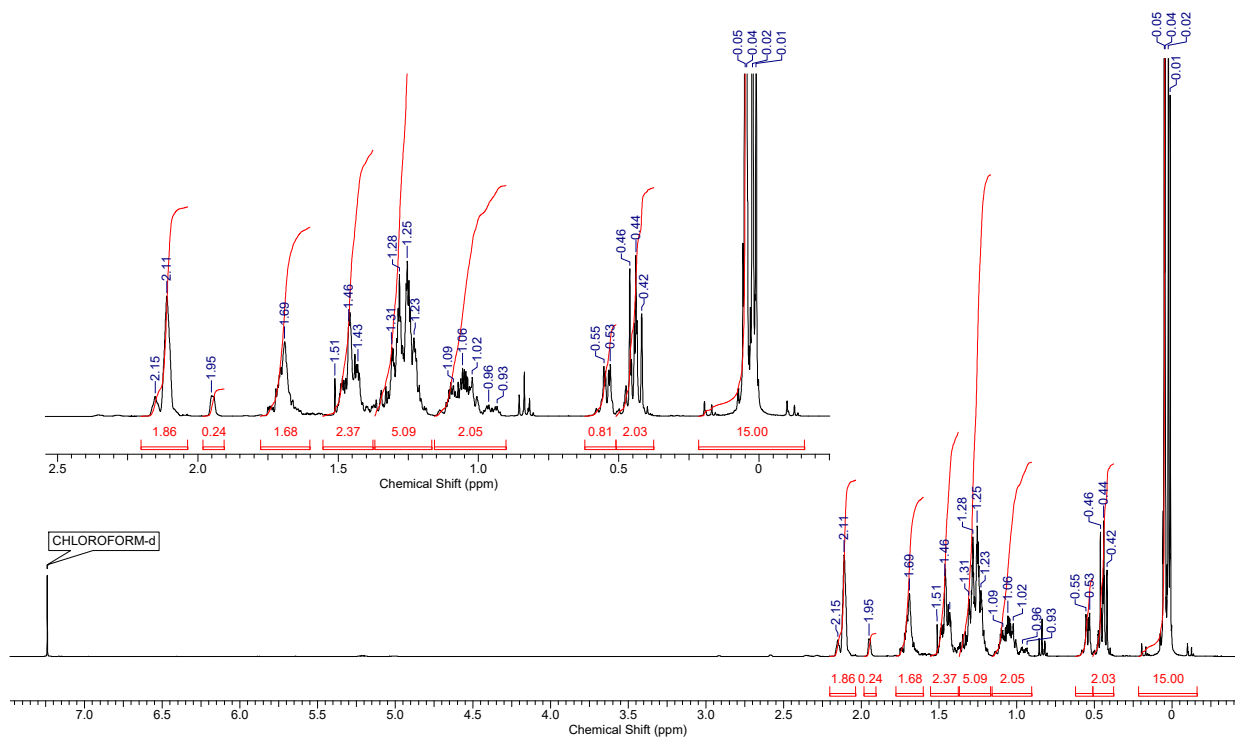


Fig. S10 ¹H NMR spectrum of PMDS-VNBA (CDCl₃).

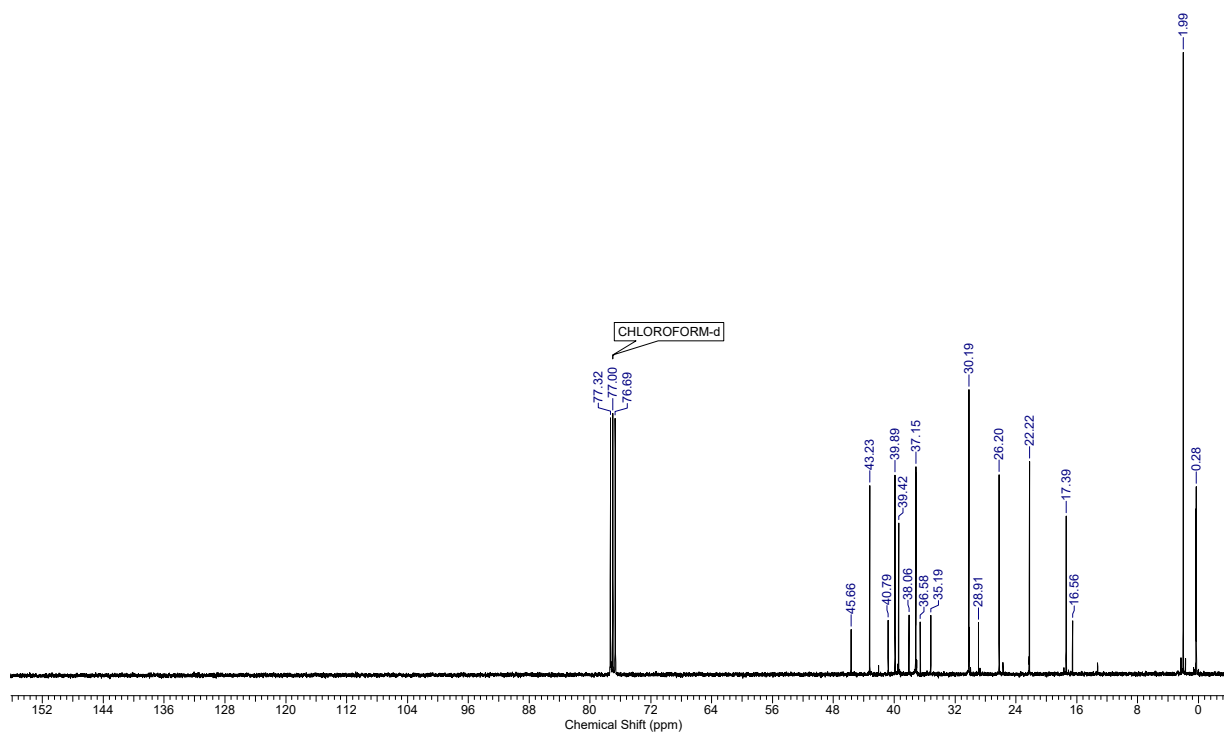


Fig. S11 ¹³C NMR spectrum of PMDS-VNBA (CDCl₃).

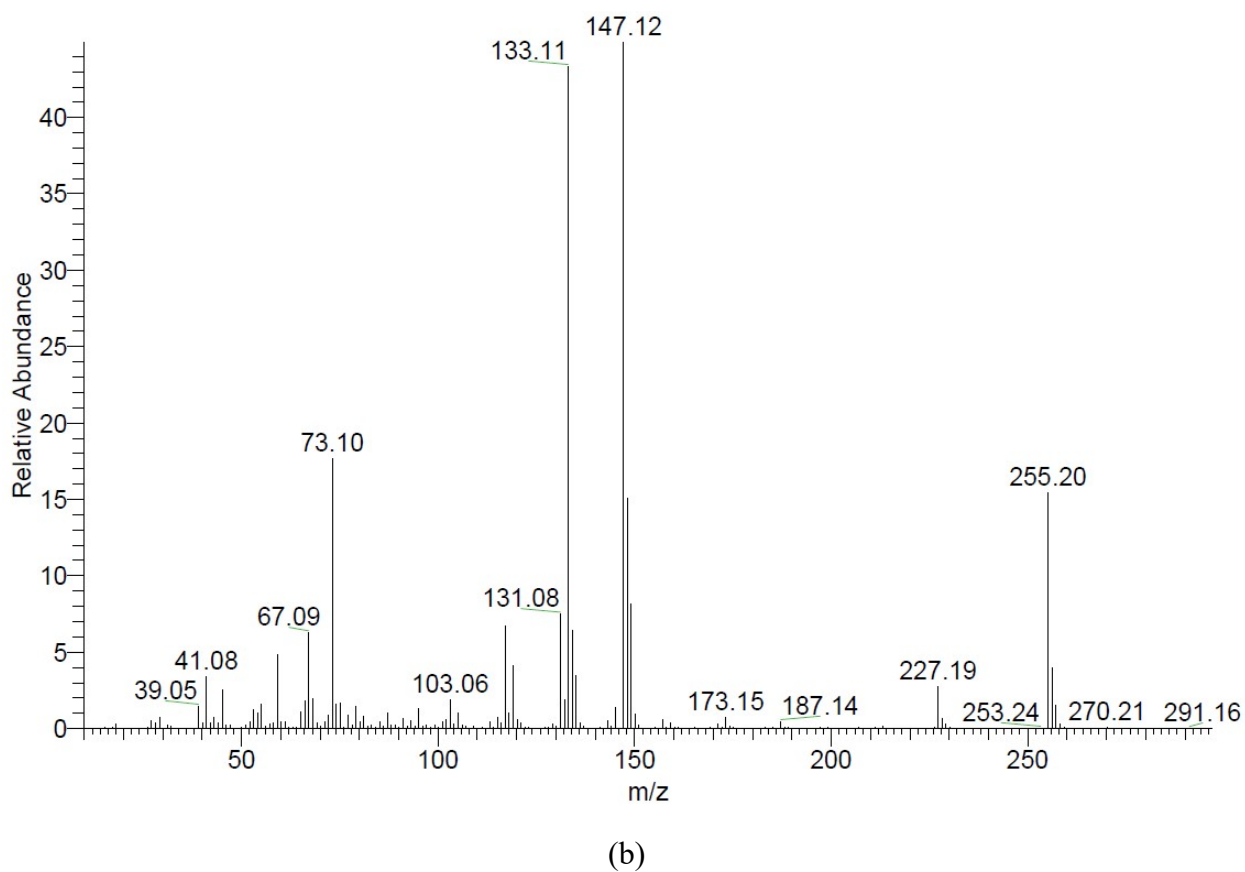
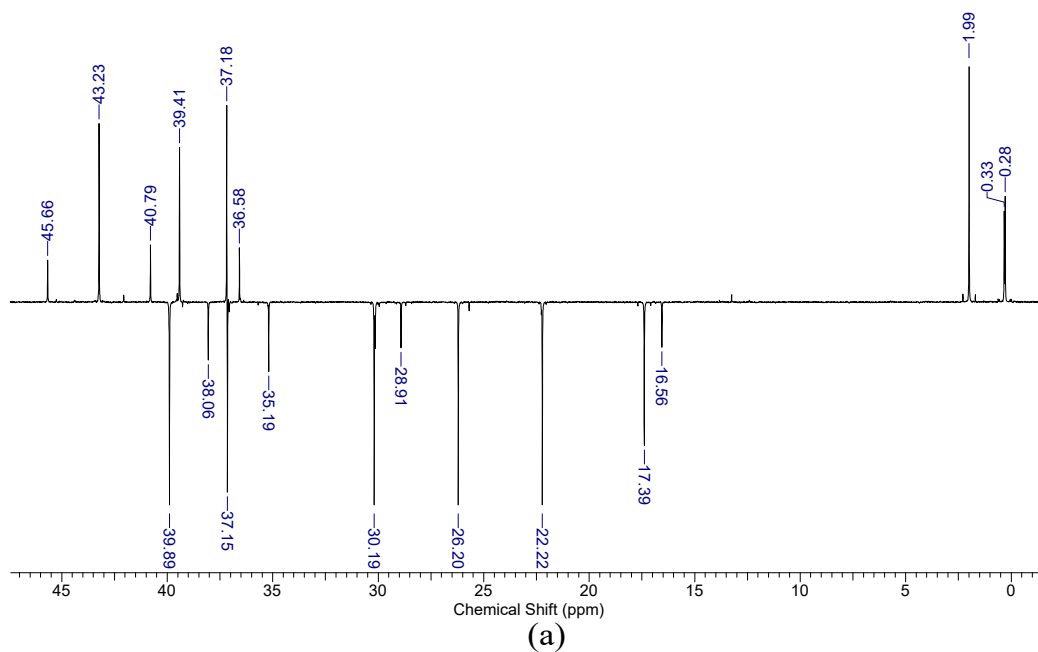


Fig. S12 (a) DEPT NMR spectrum of the product of hydrosilylation of VNBA with PMDS-H (CDCl_3); (b) Mass spectrum of PMDS-VNBA.

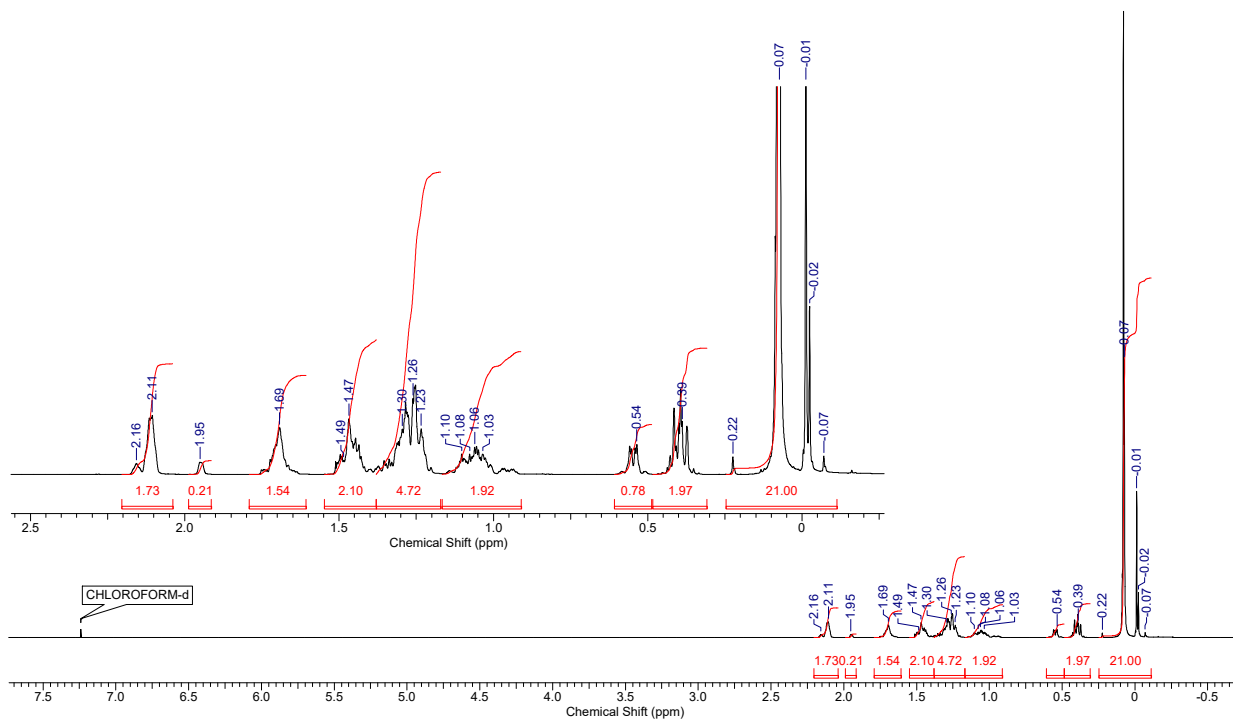


Fig. S13 ^1H NMR spectrum of HMTS-VNBA (CDCl_3).

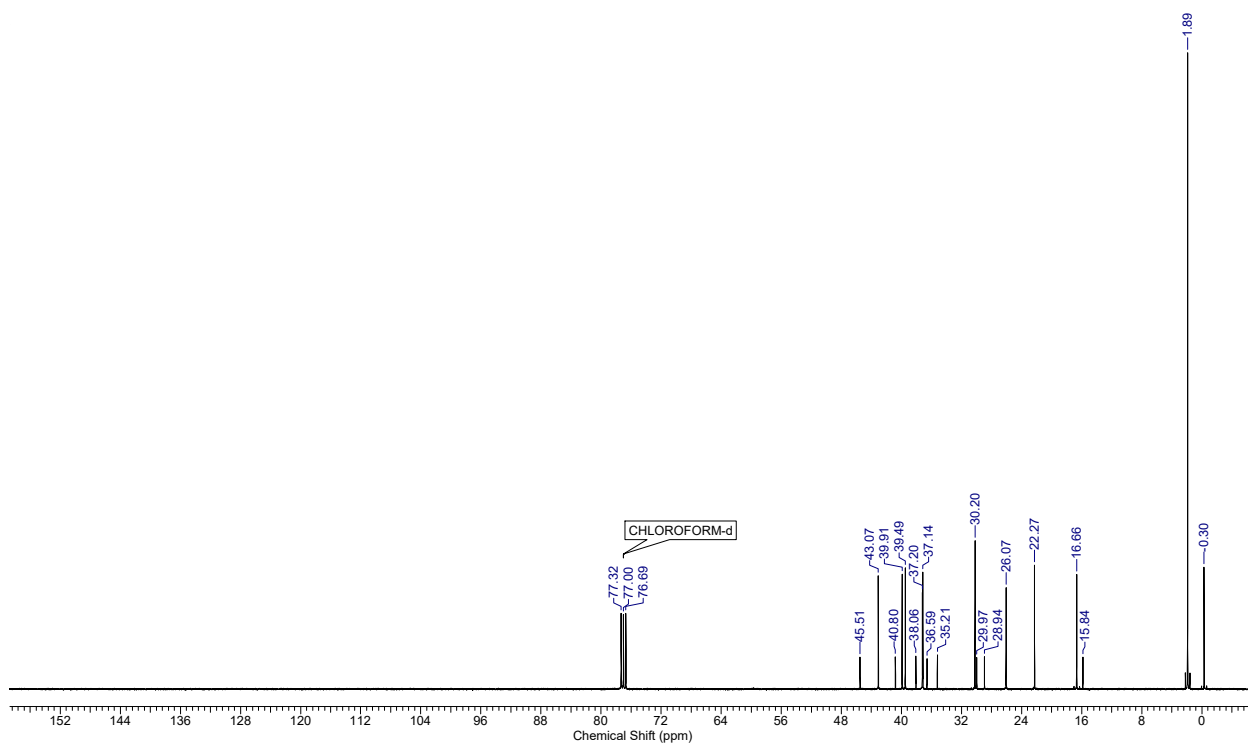


Fig. S14 ^{13}C NMR spectrum of HMTS-VNBA (CDCl_3).

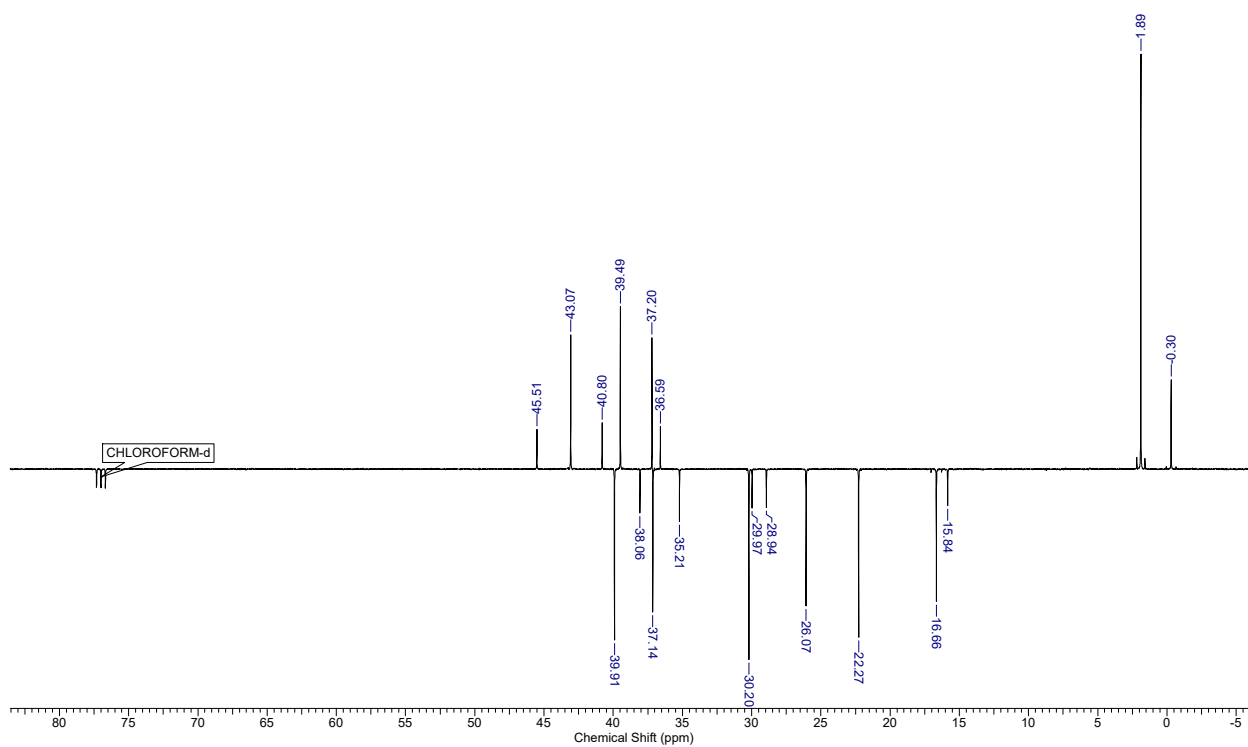


Fig. S15 DEPT NMR spectrum of HMTS-VNBA (CDCl_3).

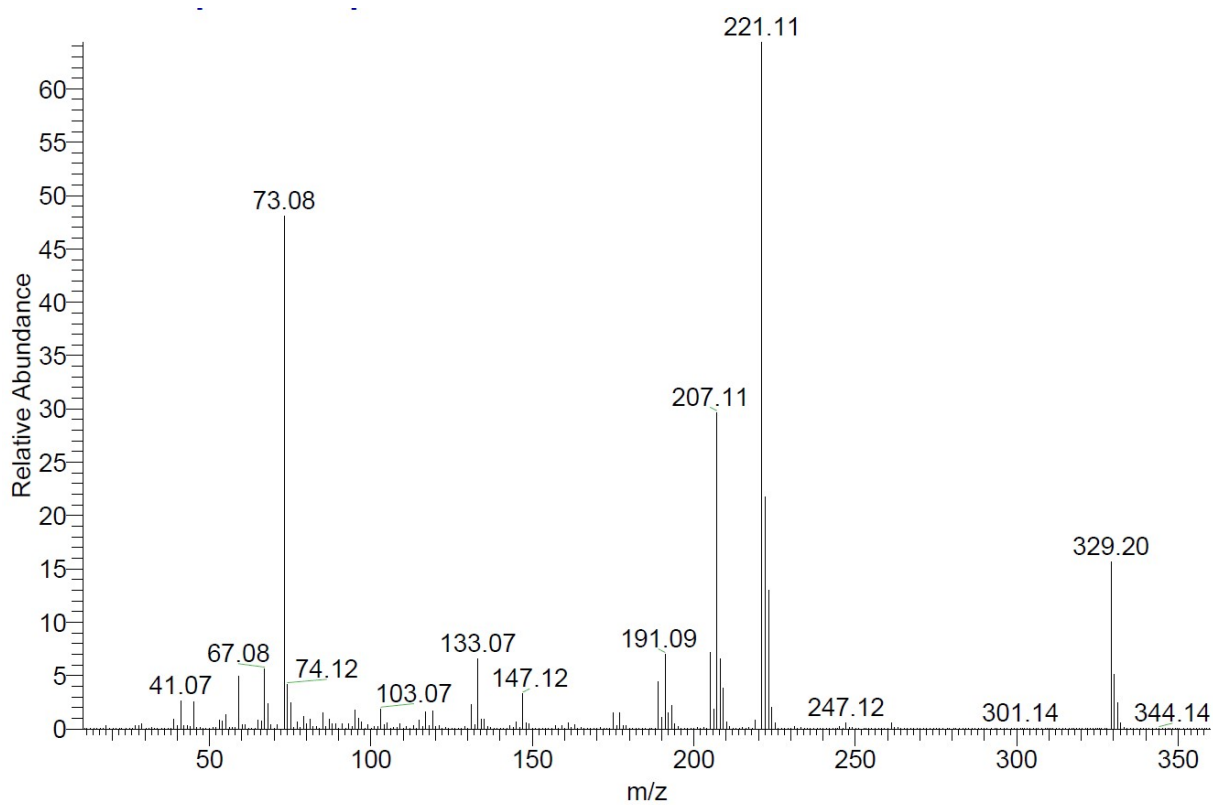


Fig. S16 Mass spectrum of HMTS-VNBA.

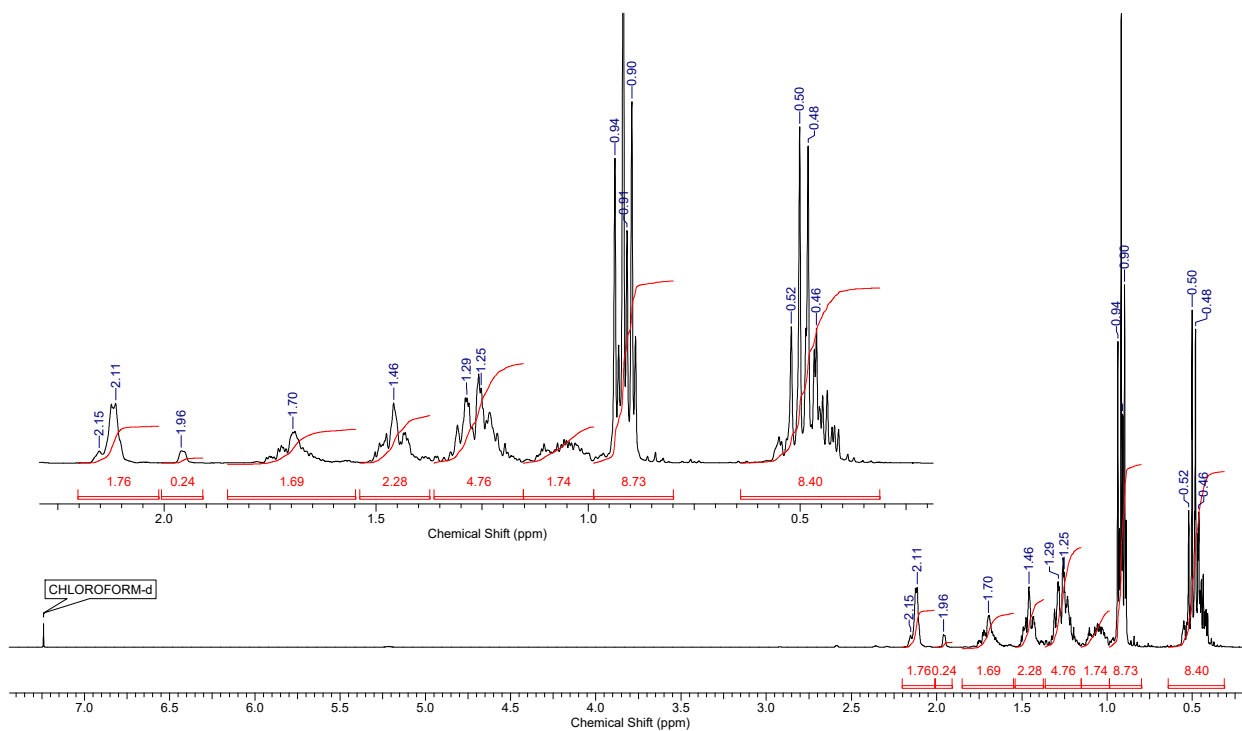


Fig. S17 ^1H NMR spectrum of $\text{Et}_3\text{Si-VNBA}$ (CDCl_3).

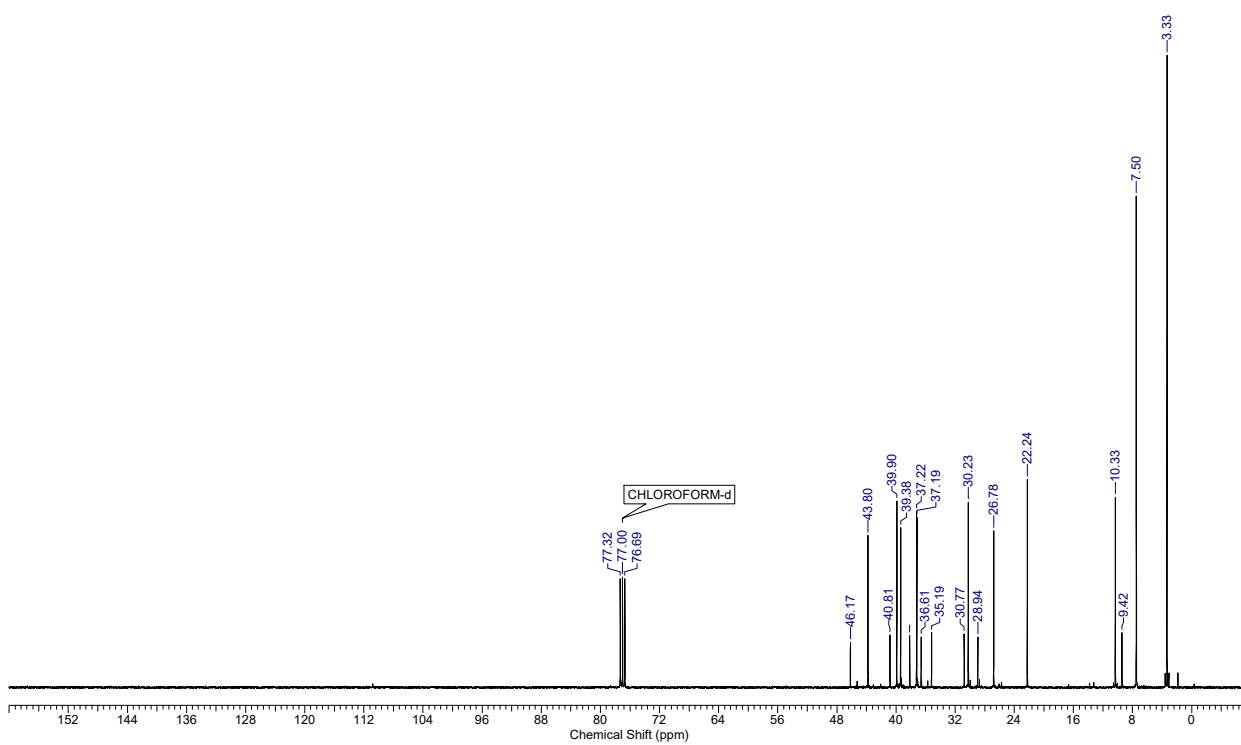


Fig. S18 ^{13}C NMR spectrum of $\text{Et}_3\text{Si-VNBA}$ (CDCl_3).

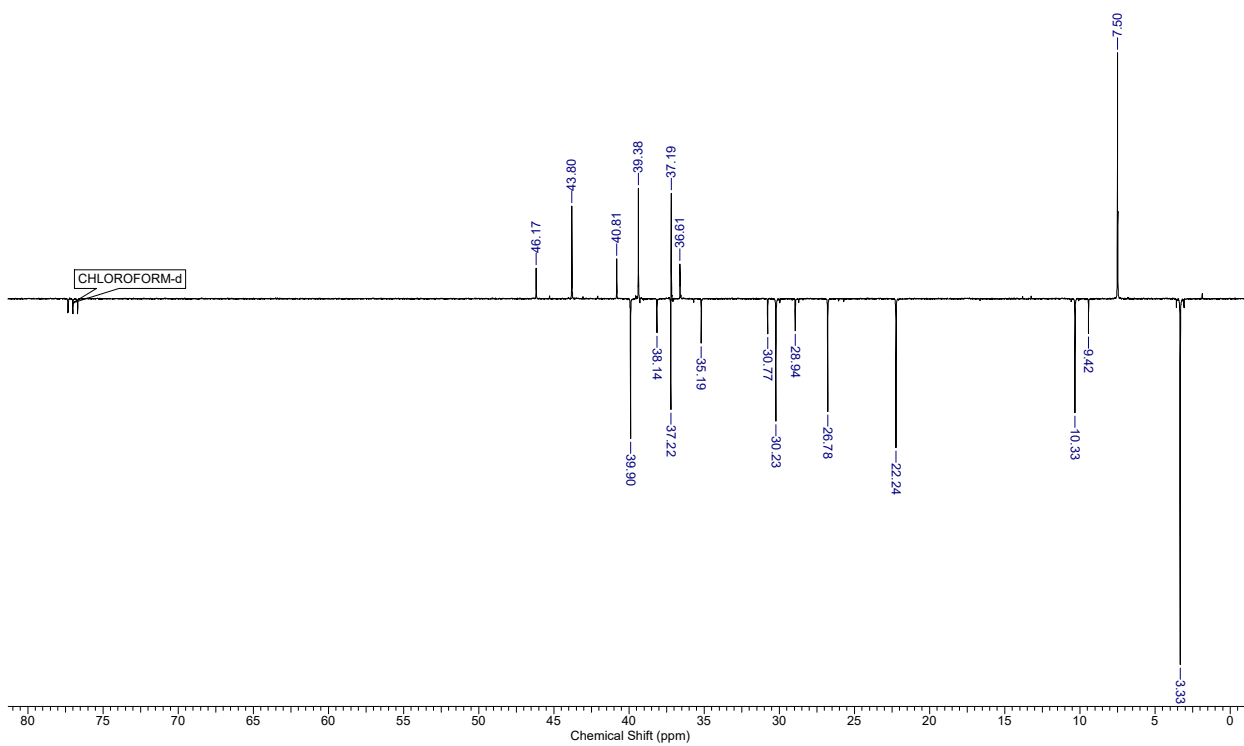


Fig. S19 DEPT NMR spectrum of $\text{Et}_3\text{Si-VNBA}$ (CDCl_3).

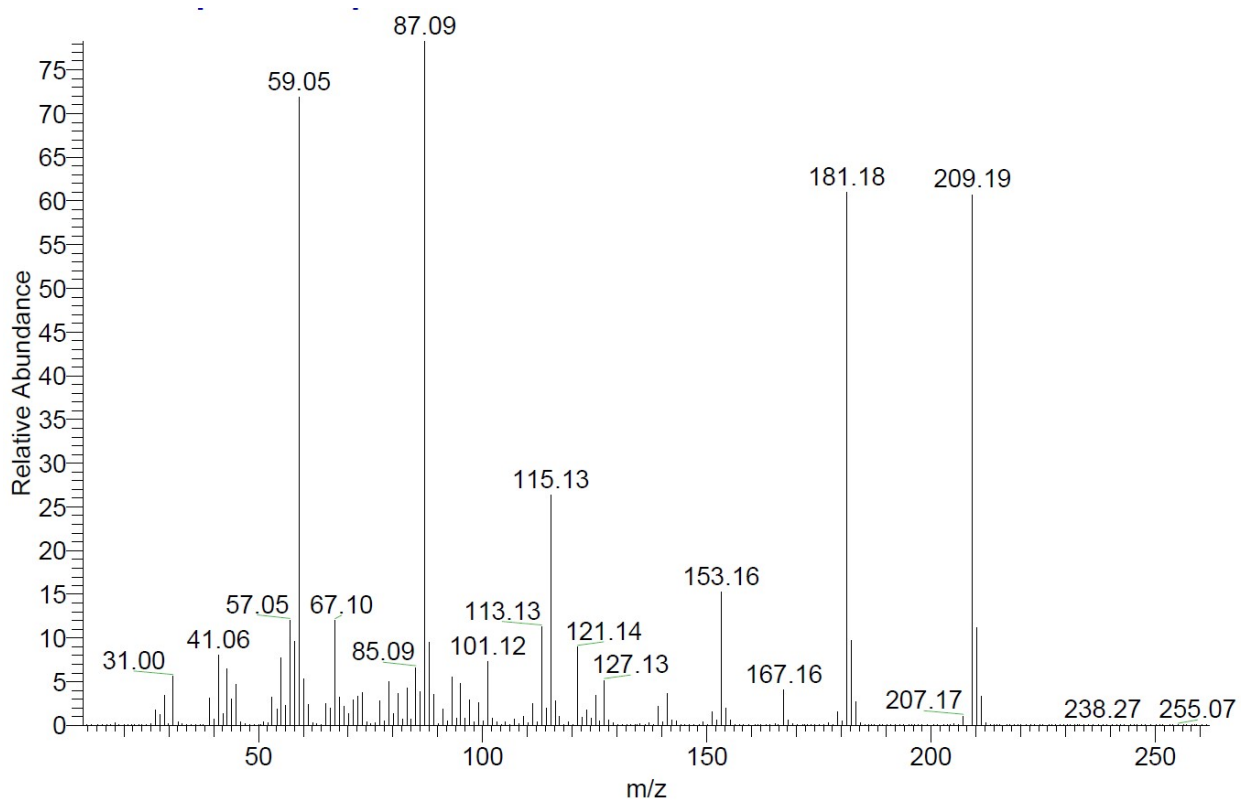


Fig. S20 Mass spectrum of Et₃Si-VNBA.

GPC curves of the modified polymers

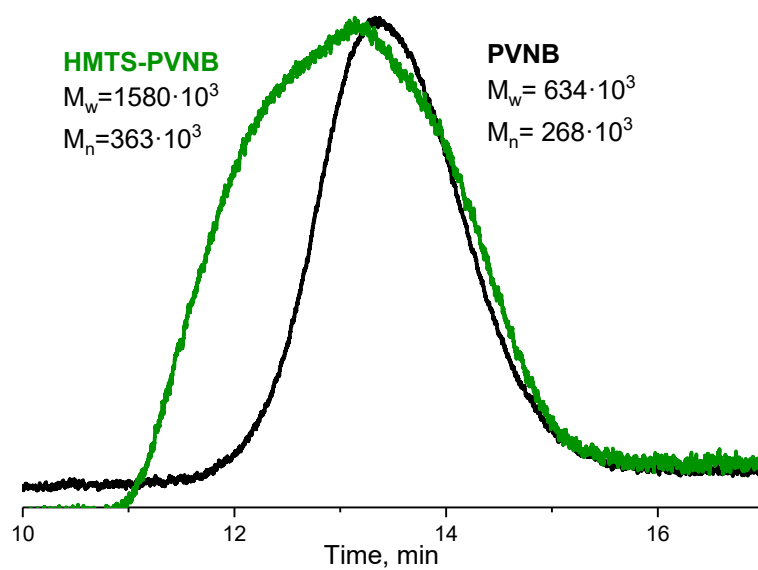


Fig. S21 GPC curves of the initial PVNB and modified PVNB by HMTS-H (HMTS-PVNB).

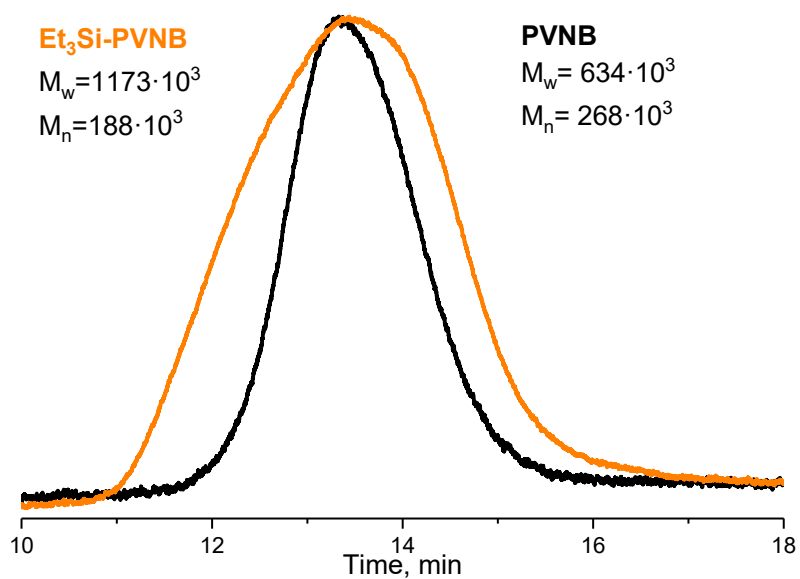


Fig. S22 GPC curves of the initial PVNB and modified PVNB by Et₃Si-H (Et₃Si-PVNB).



Fig. S23 Photos of thin films based on PVNB and modified silicon-containing polymers obtained from PVNB.

Gas permeation study for the modified vinyl-addition polynorbornenes

Table S1 Diffusivity selectivities for different pairs of gases for the modified vinyl-addition polynorbornenes in comparison with vinyl-addition polynorbornene (PNB) and PVNB.

Polymer	Diffusivity selectivity					Ref.
	O ₂ /N ₂	CO ₂ /N ₂	CO ₂ /CH ₄	H ₂ /N ₂	H ₂ /CH ₄	
PNB	3.1	2.8	11.8	113.9	482.4	1
PVNB	2.2	1.8	4.1	34.4	78.6	This work
PMDS-PVNB	1.3	1.2	1.8	13.3	20	This work
HMTS-PVNB	1.7	1.3	1.9	13.2	19.2	This work
Et ₃ Si-PVNB	2.1	1.6	3.1	31.4	61.1	This work

Table S2 Solubility selectivities for different pairs of gases for the modified vinyl-addition polynorbornenes in comparison with vinyl-addition polynorbornene (PNB) and PVNB.

Polymer	Solubility selectivity					Ref.
	O ₂ /N ₂	CO ₂ /N ₂	CO ₂ /CH ₄	H ₂ /N ₂	H ₂ /CH ₄	
PNB	1.4	7.5	1.6	0.32	0.07	1
PVNB	1.9	14.7	2.9	0.33	0.07	This work
PMDS-PVNB	1.9	11.2	2.6	0.54	0.13	This work
HMTS-PVNB	1.7	11.5	2.7	0.50	0.12	This work
Et ₃ Si-PVNB	1.6	12.3	2.7	0.33	0.07	This work

References

1. Wozniak, A. I.; Bermesheva, E. V.; Borisov, I. L.; Volkov, A. V.; Petukhov, D. I.; Gavrilova, N. N.; Shantarovich, V. P.; Asachenko, A. F.; Topchiy, M. A.; Finkelshtein, E. S.; Bermeshev, M. V., Switching on/switching off solubility controlled permeation of hydrocarbons through glassy polynorbornenes by the length of side alkyl groups. *J. Membr. Sci.* **2022**, *641*, 119848.