**Electronic Supplementary Information**

for

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

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Experimental section

Physico-Chemical Characterization

NMR spectra were recorded on spectrometers Bruker Ascend 400 at 400.1 MHz (¹H) and 100.6 MHz (¹³C) and Bruker MSL-300 at 300 MHz (¹H). Chemical shifts (δ) are reported in parts per million (ppm) relative to the reference (residual CHCl₃ signal) for ¹H and ¹³C NMR spectra. For ²⁹Si NMR spectra the proton frequency of the solvent used as reference. Each sample was dissolved in CDCl₃ 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°C/min under argon. TGA measurements were carried out on "TGA/DSC 1" (Mettler Toledo) in argon and air at the heating rate of 10 °C/min from 30 to 1000°C.

The temperature dependences of the loss tangent (tanδ) 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°C/min.

Wide-angle X-ray diffraction (WAXD) data were obtained using a two-coordinate AXS detector (Bruker, Bremen, Germany) and Cu Kα 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 (m₁). After that, the film was withdrawn, and the free wire end immersed in methanol was weighed (m₂). The density of film samples was calculated by the formula: \( d = d_S \frac{m_{dry}}{m_{dry} - (m_1 - m_2)} \), 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

Fig. S1 (a) $^1$H NMR spectra of PVNB (bottom) and PMDS-PVNB (top) in CDCl$_3$; (b) $^{13}$C NMR spectrum of PVNB (CDCl$_3$).
Fig. S2 (a) $^{13}$C and DEPT-135 NMR spectra of PMDS-PVNB in CDCl$_3$; (b) $^{29}$Si NMR spectrum of PMDS-PVNB (CDCl$_3$).
Fig. S3 $^1$H 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** $^1$H NMR spectrum of Et$_3$Si-PVNB (CDCl$_3$).

**Fig. S8** $^{13}$C NMR spectrum of Et$_3$Si-PVNB (CDCl$_3$).
Fig. S9 $^{29}$Si NMR spectrum of Et$_3$Si-PVNB (CDCl$_3$).
NMR and Mass spectra of the hydrosilylated products of VNBA

Fig. S10 $^1$H NMR spectrum of PMDS-VNBA (CDCl$_3$).

Fig. S11 $^{13}$C NMR spectrum of PMDS-VNBA (CDCl$_3$).
Fig. S12 (a) DEPT NMR spectrum of the product of hydrosilylation of VNBA with PMDS-H (CDCl₃); (b) Mass spectrum of PMDS-VNBA.
Fig. S13 $^1$H 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 $^1$H NMR spectrum of Et$_3$Si-VNBA (CDCl$_3$).
Fig. S18 $^{13}$C NMR spectrum of Et$_3$Si-VNBA (CDCl$_3$).

Fig. S19 DEPT NMR spectrum of Et$_3$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.

<table>
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<th>Polymer</th>
<th>O$_2$/N$_2$</th>
<th>CO$_2$/N$_2$</th>
<th>CO$_2$/CH$_4$</th>
<th>H$_2$/N$_2$</th>
<th>H$_2$/CH$_4$</th>
<th>Ref.</th>
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<td>11.8</td>
<td>113.9</td>
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<tr>
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<td>PMDS-PVNB</td>
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<td>20</td>
<td>This work</td>
</tr>
<tr>
<td>HMTS-PVNB</td>
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<td>1.3</td>
<td>1.9</td>
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<td>Et$_3$Si-PVNB</td>
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<td>3.1</td>
<td>31.4</td>
<td>61.1</td>
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Table S2 Solubility selectivities for different pairs of gases for the modified vinyl-addition polynorbornenes in comparison with vinyl-addition polynorbornene (PNB) and PVNB.

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<thead>
<tr>
<th>Polymer</th>
<th>O$_2$/N$_2$</th>
<th>CO$_2$/N$_2$</th>
<th>CO$_2$/CH$_4$</th>
<th>H$_2$/N$_2$</th>
<th>H$_2$/CH$_4$</th>
<th>Ref.</th>
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<td>PVNB</td>
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<td>0.12</td>
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<td>2.7</td>
<td>0.33</td>
<td>0.07</td>
<td>This work</td>
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References