Supporting Information

Fine-tuning of the dielectric properties of polysiloxanes by chemical modification

Simon J. Dünki,1,2 Martin Tress,3 Friedrich Kremer,3* Song Yee Ko,1,2 Frank A. Nüesch,1,2 Cristian-Dragos Varganici,4 Carmen Račes,4* Dorina M. Opris1*

P2: 1H NMR (CDCl3, δ): 2.60 – 2.48 (m, 4H, -CH2-S-CH2-), 1.60 – 1.52 (m, 2H, CH2-CH2-CH3), 1.46 – 1.37 (m, 2H, CH2-CH3), 0.94 – 0.87 (m, 5H, Si-CH2-, CH2-CH3). 0.14 (s, 3H, Si-CH3); 13C NMR (CDCl3, δ): 31.9, 31.8, 22.2, 18.5, 13.9, 0.1; 29Si NMR (CDCl3, δ) 24.0; EA: Calcd.: C 47.68, H 9.14, S 18.18; found C 47.56, H 9.11, S 17.95.

P29P31: 1H NMR (CDCl3, δ): 2.83 – 2.78 (m, 2H, CH2-CH2-CN), 2.69 – 2.62 (m, 4H, CH2-S-CH2-CH2-CN), 2.59 – 2.49 (m, 36H, CH2-S-CH2-Pr), 1.61 – 1.52 (m, 18H, CH2-CH2-CH3), 1.46 – 1.36 (m, 18H, CH2-CH3), 0.95 – 0.86 (m, 47H, Si-CH2-, CH2-CH3). 0.14 (s, 30H, Si-CH3); 13C NMR (CDCl3, δ): 118.4, 31.82, 31.76, 27.7, 26.8, 26.5, 22.2, 19.0, 18.4, 18.2, 13.8, 0.0; 29Si NMR (CDCl3, δ) 24.0; EA: Calcd.: C 47.08, H 8.87, N 0.8, S 18.21; found: C 48.42, H 8.72, N 1.62, S 17.78.

P28P32: 1H NMR (CDCl3, δ): 2.83 – 2.77 (m, 4H, CH2-CH2-CN), 2.69 – 2.62 (m, 8H, CH2-S-CH2-CH2-CN), 2.59 – 2.49 (m, 32H, CH2-S-CH2-Pr), 1.60 – 1.51 (m, 16H, CH2-CH2-CH3), 1.45 – 1.35 (m, 16H, CH2-CH3), 0.95 – 0.85 (m, 44H, Si-CH2-, CH2-CH3). 0.14 (s, 30H, Si-CH3); 13C NMR (CDCl3, δ): 118.5, 31.84, 31.77, 27.7, 26.8, 26.5, 22.2, 19.0, 18.5, 18.2, 13.8, 0.1; 29Si NMR (CDCl3, δ) 24.0; EA: Calcd.: C 46.47, H 8.60, N 1.59, S 18.25; found: C 46.23, H 8.84, N 1.65, S 18.05.

P27P33: 1H NMR (CDCl3, δ): 2.84 – 2.77 (m, 6H, CH2-CH2-CN), 2.70 – 2.62 (m, 12H, CH2-S-CH2-CH2-CN), 2.58 – 2.47 (m, 28H, CH2-S-CH2-Pr), 1.60 – 1.51 (m, 14H, CH2-CH2-CH3),
1.46 – 1.35 (m, 14H, CH₂-CH₃), 0.96 – 0.85 (m, 41H, Si-CH₂-, CH₂-CH₃). 0.14 (s, 30H, Si-CH₃); ¹³C NMR (CDCl₃, δ): 118.5, 31.86, 31.78, 27.7, 26.9, 26.5, 22.2, 19.1, 18.5, 18.2, 13.9, 0.1; ²⁹Si NMR (CDCl₃, δ): 24.6, 23.8; EA: Calcd.: C 45.87, H 8.33, N 2.40, S 18.28; found: C 45.71, H 8.48, N 2.46, S 17.99.

P₂₆P₃₄: ¹H NMR (CDCl₃, δ): 2.85 – 2.77 (m, 8H, CH₂-CH₂-CN), 2.70 – 2.61 (m, 16H, CH₂-S-CH₂-CH₃-CN), 2.58 – 2.48 (m, 24H, CH₂-S-CH₂-Pr), 1.60 – 1.51 (m, 12H, CH₂-CH₂-CH₃), 1.46 – 1.35 (m, 12H, CH₂-CH₃), 0.97 – 0.85 (m, 38H, Si-CH₂-, CH₂-CH₃). 0.14 (s, 30H, Si-CH₃); ¹³C NMR (CDCl₃, δ): 118.6, 31.9, 31.8, 27.7, 26.8, 26.5, 22.2, 19.1, 18.4, 18.2, 13.8, 0.1; ²⁹Si NMR (CDCl₃, δ): 24.6, 23.6; EA: Calcd.: C 45.26, H 8.06, N 3.20, S 18.31; found: C 43.40, H 8.12, N 3.16, S 18.29.

P₂₇P₃₁: ¹H NMR (CDCl₃, δ): 2.85 – 2.76 (m, 2H, CH₂-CH₂-CN), 2.73 – 2.61 (m, 4H, CH₂-S-CH₂-CH₂-CN), 2.58 – 2.48 (m, 4H, CH₂-S-CH₂-Pr), 1.60 – 1.51 (m, 2H, CH₂-CH₂-CH₃), 1.46 – 1.35 (m, 2H, CH₂-CH₃), 0.98 – 0.85 (m, 7H, Si-CH₂-, CH₂-CH₃). 0.15 (s, 6H, Si-CH₃); ¹³C NMR (CDCl₃, δ): 118.6, 31.9, 31.8, 27.7, 26.8, 26.4, 22.2, 19.1, 18.4, 18.2, 13.8, 0.1; ²⁹Si NMR (CDCl₃, δ): 24.6, 23.7; EA: Calcd.: C 44.66, H 7.78, N 4.01, S 18.34; found: C 42.59, H 7.95, N 3.76, S 18.36.

P₂₈P₃₆: ¹H NMR (CDCl₃, δ): 2.85 – 2.77 (m, 12H, CH₂-CH₂-CN), 2.73 – 2.63 (m, 24H, CH₂-S-CH₂-CN), 2.59 – 2.49 (m, 16H, CH₂-S-CH₂-Pr), 1.60 – 1.51 (m, 8H, CH₂-CH₂-CH₃), 1.46 – 1.35 (m, 8H, CH₂-CH₃), 0.97 – 0.86 (m, 32H, Si-CH₂-, CH₂-CH₃). 0.16 (s, 30H, Si-CH₃); ¹³C NMR (CDCl₃, δ): 118.7, 31.9, 31.8, 27.7, 26.8, 26.5, 22.2, 19.2, 18.4, 18.3, 13.9, 0.1; ²⁹Si NMR (CDCl₃, δ): 24.2, 23.4; EA: Calcd.: C 44.04, 7.51. N 4.82, S 18.37; found: C 42.03, H 7.65, N 4.65, S 17.60.
**P2, P3:** $^1$H NMR (CDCl$_3$, $\delta$): 2.85 – 2.78 (m, 14H, CH$_2$=CH$_2$-CN), 2.73 – 2.64 (m, 28H, CH$_2$-S-CH$_2$-CH$_2$-CN), 2.58 – 2.49 (m, 12H, CH$_2$-S-CH$_2$-Pr), 1.60 – 1.52 (m, 6H, CH$_2$-CH$_2$-CH$_3$), 1.46 – 1.36 (m, 6H, CH$_3$), 0.97 – 0.87 (m, 41H, Si-CH$_2$, CH$_3$-CH$_3$), 0.17 (s, 30H, Si-CH$_3$); $^{13}$C NMR (CDCl$_3$, $\delta$): 118.7, 31.9, 31.8, 27.7, 26.8, 26.5, 22.2, 19.2, 18.4, 18.3, 13.9, 0.1; $^{29}$Si NMR (CDCl$_3$, $\delta$): 24.2, 23.2; EA: Calcd.: C 43.43, H 7.23, N 5.63, S 18.4; found: C 41.17, H 6.49, N 5.77, S 16.61.

**P3:** $^1$H NMR (CDCl$_3$, $\delta$): 2.85 – 2.78 (m, 2H, CH$_2$=CH$_2$-CN), 2.72 – 2.64 (m, 4H, CH$_2$-S-CH$_2$-CH$_2$-CN), 0.95 – 0.88 (m, 2H, Si-CH$_2$-), 0.18 (s, 3H, Si-CH$_3$); $^{13}$C NMR (CDCl$_3$, $\delta$): 118.8, 27.5, 26.6, 19.0, 18. 0.0; $^{29}$Si NMR (CDCl$_3$, $\delta$): 24.2; EA: Calcd.: C 41.58, H 6.40, N 8.08, S 18.5; found C 39.47, H 6.49, N 8.04, S 17.63.

The deviations of the data from combustion analysis with the calculated ones for some of the samples is likely due to some residual solvents that were difficult to remove from the highly viscous polymers. For the amount of methanol left in the samples, see Table 1.
Fig. S1a $^1$H NMR spectra of P2, P3, and P2$_x$P3$_y$. 
Fig. S1b $^1$H NMR spectrum of P2$_1$P3$_1$ with assignment of the peaks to the corresponding protons. Peaks denominated with an * are assigned to the Markovnikov addition product.
Fig. S2 $^{13}$C NMR spectra of $P_1$, $P_2$, $P_3$ and $P_{21}P_{31}$ (top) and of $P_{21}P_{31}$ with assignment of the peaks (bottom).
Fig. S3 $^{13}$C NMR spectra of P2, P3, and P2xP3.
Fig. S4 $^1$H-$^1$H-DQF-COSY NMR spectrum of $P_2P_3$ (top); $^1$H-$^{13}$C-HMBC NMR spectrum of $P_2P_3$ (middle); $^1$H-$^{13}$C-HSQC NMR spectrum of $P_2P_3$ (bottom).
**Fig. S5** The IR spectra of P1, P2, P2<sub>1</sub>P3<sub>1</sub>, and P3.

**Fig. S6** The glass transition temperatures of P2, P3, P2<sub>x</sub>P3<sub>y</sub> (left). A linear increase in the $T_g$ with increasing the amount of nitrile groups was observed. Cp of P2, P3, P2<sub>x</sub>P3<sub>y</sub> as function of mol% of polar nitrile group (right).
Fig. S7 The enlargement of the DSC heating scans in the melting region of the crystalline domains of P2, P3 and P2-xP3-y.

Fig. S8 GPC elugrams in tetrahydrofuran (left) and TGA (right) of P2, P3, and P2-xP3-y. The elugrams of P2, P3, and P2-xP3-y were integrated from 10.5 ml to 13.5 ml.

A composition of up to four Havriliak-Negami functions [Havriliak, S. & Negami, S. Polymer, 1967, 8, 161] for the α-relaxation (segmental motion) in the amorphous phase, the alpha-relaxation of segments neighbouring crystalline domains and the local fluctuations of the methyl- and nitrile-terminated side chains, respectively (each accounted for by the index j in the following equation) and a term accounting for conductivity [Kremer, F. & Schönhals, A. (Eds.) Broadband Dielectric Spectroscopy Springer, Berlin Heidelberg, 2003] has been employed to fit the dielectric loss spectra $\varepsilon''(f)$

$$
\varepsilon''(\omega) = \sum_{j=1}^{4} -\text{Im} \left\{ \frac{\Delta \varepsilon_j}{(1 + i(\omega \tau_{HN,j})^{\delta_j})^{\delta_j}} \right\} + \frac{\alpha \sigma_{DC}}{\varepsilon_0 \omega} 
$$

Equation S1
with the angular frequency $\omega=2\pi f$, the symbol for the imaginary part $\text{Im}$ and the imaginary unit $i=(-1)^{0.5}$. Four parameters describe the imaginary part of the Havriliak-Negami function: the dielectric relaxation strength $\Delta\varepsilon$, the relaxation time $\tau_{HN}$ and the parameters for symmetric and asymmetric broadening $\alpha$ and $\beta$, respectively. The conductivity contribution consists of the DC-conductivity $\sigma_{DC}$, the exponent $s$ ($0<s\leq1$) and the parameter $a=(1\text{ Hz})^{-1}$ to correct for the units. $\varepsilon_0$ denotes the permittivity of the vacuum. Note that for fitting each single temperature, only those components (number of Havriliak-Negami functions, conductivity contribution) which are present in the respective loss spectrum were included in the composed fit function.

![Graph showing dielectric loss as a function of frequency at different temperatures for polymer P2. Solid lines represent fits of equation 1 to the data.]

**Fig. S9** Dielectric loss as a function of frequency of polymer P2 at different temperature as indicated. Solid lines represent fits of equation 1 to the data.

The mean relaxation time $\tau$ indicating the peak position in the spectra can be calculated from the relaxation time $\tau_{HN}$ and the parameters for symmetric and asymmetric broadening $\alpha$ and $\beta$ extracted from Equation S1

$$\tau = \tau_{HN} \left( \frac{\sin \left( \frac{\beta \pi}{2+2\gamma} \right)}{\sin \left( \frac{\beta \pi}{2+2\gamma} \right)} \right)^{\frac{1}{\gamma}}$$  \hspace{1cm} \text{Equation S2}
Fig. S10 Dielectric permittivity ($\varepsilon'$) and loss ($\varepsilon''$) as well as the real and imaginary part of the complex conductivity ($\sigma'$ and $\sigma''$, respectively) of the sample P2, P3 as a function of frequency for different temperatures as indicated.

To analyze the temperature dependence of the mean relaxation rates, two equations were employed. First, primary relaxations (the α-relaxations) follow the Vogel-Fulcher-Tammann equation [Vogel, H. Physikalische Zeitschrift, 1921, 22, 645; Fulcher, G. S. Journal of the American Chemical Society, 1925, 8, 339; Tammann, G. & Hesse, G. Zeitschrift für anorganische und allgemeine Chemie, 1926, 156, 245] which is characteristic for glassy systems

$$\tau(T) = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right)$$

Equation S3

with the relaxation relaxation time in the infinite temperature limit $\tau_0$, the so-called fragility parameter $D$ and the Vogel temperature $T_0$.

Second, the secondary relaxations, i.e. local fluctuations of side chains, typically exhibit a thermal activation $\tau(T)$ according to the Arrhenius equation

$$\tau(T) = \tau_0 \exp\left(\frac{E_A}{RT}\right)$$

Equation S4
where $\tau_0$ denotes the relaxation time in the infinite temperature limit, $E_a$ the activation energy and $R=8.314 \text{ J(mol K)}^{-1}$ the universal gas constant.

**Fig. S11** Activation plot of the mean relaxation times $\tau$ extracted from the dielectric loss spectra (Fig. S9) of sample P2, P3. Two primary relaxations can be identified according to their Vogel-Fulcher-Tammann temperature dependence (Equation S3), which coincide with the calorimetric glass transition as determined by DSC, as well as a secondary relaxation which exhibits an Arrhenius type activation (Equation S4). The error bars indicate the uncertainty of the fit parameters; in the primary relaxations, this uncertainty is larger due to the proximity of these two processes.
Fig. S12 Dielectric permittivity ($\varepsilon'$) and loss ($\varepsilon''$) as well as the real and imaginary part of the complex conductivity ($\sigma'$ and $\sigma''$, respectively) of the sample P3 as a function of frequency for different temperatures as indicated.
**Fig. S13** Activation plot of the mean relaxation times $\tau$ extracted from the dielectric loss spectra (Fig. S12) of sample P3. Two primary relaxations can be identified according to their Vogel-Fulcher-Tammann temperature dependence (Equation S3), which coincide with the calorimetric glass transition as determined by DSC, as well as a secondary relaxation which exhibits an Arrhenius type activation (Equation S4). The error bars indicate the uncertainty of the fit parameters; in the primary relaxations, this uncertainty is larger due to the proximity of these two processes.

**Table S1** VFT fit parameters of the $\alpha$-relaxation of the siloxane backbone and the slower primary relaxation of unclear origin according to Equation S3. For the amorphous $\alpha$-relaxation, also the expected glass transition temperature $T_g$ is given by extrapolating the VFT fit to a mean relaxation time of $\tau=100s$.

<table>
<thead>
<tr>
<th>sample</th>
<th>$\tau_0$ [s]</th>
<th>$D$</th>
<th>$T_0$ [K]</th>
<th>$T_g$ [°C]</th>
<th>$\tau_0$ [s]</th>
<th>$D$</th>
<th>$T_0$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>2 ($\pm$9) $10^{-17}$</td>
<td>13.7 ($\pm$4.9)</td>
<td>109 ($\pm$7)</td>
<td>2.4 ($\pm$3.8)</td>
<td>1 ($\pm$11) $10^{-7}$</td>
<td>135 ($\pm$21)</td>
<td></td>
</tr>
<tr>
<td>P2</td>
<td>1.9 ($\pm$1.8) $10^{-12}$</td>
<td>5.6 ($\pm$0.7)</td>
<td>146 ($\pm$2)</td>
<td>8.1 ($\pm$2.0)</td>
<td>7.6 ($\pm$8.9) $10^{-11}$</td>
<td>128 ($\pm$7)</td>
<td></td>
</tr>
</tbody>
</table>
Table S2 Arrhenius fit parameters of the local fluctuations of the methyl-terminated and the nitrile-terminated side chains, respectively according to Equation S4.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Terminal Group</th>
<th>( \tau_0 ) [s]</th>
<th>( E_A ) [kJ/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2</td>
<td>methyl</td>
<td>7.0 (±0.6) ( 10^{-15} )</td>
<td>23.2 (±0.1)</td>
</tr>
<tr>
<td>P2₁P3₁</td>
<td>methyl</td>
<td>1.3 (±0.9) ( 10^{-15} )</td>
<td>27.0 (±0.7)</td>
</tr>
<tr>
<td>P2₁P3₁</td>
<td>nitrile</td>
<td>7 (±15) ( 10^{-21} )</td>
<td>55.1 (±3.1)</td>
</tr>
<tr>
<td>P3</td>
<td>nitrile</td>
<td>3.2 (±0.6) ( 10^{-18} )</td>
<td>51.8 (±0.3)</td>
</tr>
</tbody>
</table>

Fig. S14 Dielectric properties: permittivity (\( \varepsilon' \)), dielectric loss (\( \varepsilon'' \)), conductivity (\( \sigma \)), loss factor (\( \tan \delta \)) of polymers P2, P3 and P2₁P3₁.
Fig. S15 Dependence of the real part (G') and imaginary (G'') parts of the shear modulus and the loss angle tan (δ) for a material prepared by cross-linking P3 as a function of frequency and room temperature.

Fig. S16 Stress-strain curves of an elastomer prepared starting from P3 by crosslinking via the hydroxyl end-groups.