Electronic Supporting Information

Synthesis of a Self-Healing Siloxane-Based Elastomer Cross-Linked via a Furan-Modified Polyhedral Oligomeric Silsesquioxane: Investigation of a Thermally Reversible Silicon-Based Cross-Link

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Figure 1. $^1$H NMR spectrum of compound 3.

Figure 2. $^{13}$C NMR spectrum of compound 3.
Figure 3. $^{29}$Si NMR spectrum of compound 3.

Figure 4. $^1$H NMR spectrum of compound 5.
Figure 5. $^{13}$C NMR spectrum of compound 5.

Figure 6. $^{29}$Si NMR spectrum of compound 5.
Figure 7. $^1$H NMR spectrum of compound 8.

Figure 8. $^{13}$C NMR spectrum of compound 8.
Figure 9. $^1H$ NMR spectrum of compound 10.

Figure 10. $^{13}C$ NMR spectrum of compound 10.
Figure 11. $^{29}$Si NMR spectrum of compound 10.

Figure 12. $^1$H NMR spectrum of PDMS-2.
Figure 13. $^{13}$C NMR spectrum of PDMS-2.

Figure 14. $^{29}$Si NMR spectrum of PDMS-2.
Figure 15. $^1$H NMR spectrum of PDMS-3.

Figure 16. $^{13}$C NMR spectrum of PDMS-3.
**Figure 17.** $^{29}$Si NMR spectrum of PDMS-3.

**Figure 18.** $^1$H NMR spectrum of compound 12.
**Figure 19.** $^{13}$C NMR spectrum of compound 12.

**Figure 20.** $^{29}$Si NMR spectrum of compound 12.
Figure 21. MALDI-ToF mass spectrometry of 12.

Sample Prep: Acetone/NaAc/DITH
Ion Source: MALDI
Measured mass: 3152.363 m/z
Theoretical mass of [C144H248O44Si16+Na]+: 3152.337 m/z
\( \Delta m/m = 8.2 \text{ppm} \)

Figure 22. ATR-IR spectrums of the diene (10), the dienophile (5) and a DA reaction mixture which contained 88% adduct (11) according to \(^1\)H NMR.
Figure 23. $^1$H NMR spectroscopy of a Diels-Alder reaction mixture containing 10, 5, and 11.
**Figure 24.** gCOSY NMR spectroscopy of a Diels-Alder reaction mixture. Only the endo isomer correlates with the bridge’s hydrogen.

**Figure 25.** A series of $^1$H NMR spectra acquired for sample B in different time periods and various temperatures followed subsequently.
**Figure 26.** A series of $^1$H NMR spectra acquired for sample A in different time periods and various temperatures followed subsequently.

**Figure 27.** $^1$H NMR spectra of a DA mixture sample contained a high quantity of the adduct (11) before and after exposing to 136°C for 2 min.