Supplementary Information

The supplementary information contain:

- The deconvolution of spectra in individual components
- Equations used for the quantifications

Figure S1. Quantitative $^{29}$Si echo-MAS NMR spectra (in blue) collected for the studied hybrid glasses. In red are models obtained for each sample from a simultaneous fit of multiple spectra (including $^{29}$Si echo-MAS with different recycling delays and $^{29}$Si[$^1$H] CP-MAS spectra with different contact times, not shown) with a single set of parameters (number of peaks, positions, width and Gaussian/Lorentzian ratio). The individual components used for the fits are shown in black below.
Equations used for the quantifications.

Fixing an arbitrary number of C atoms $n_{C,tot}$ (e.g. $n_{C,tot} = 100$), one can then derive the number of carbons attributed to $\text{Me}_2\text{Si}$ and $\text{MeSi}$ groups that can be expected based on the ratios of MTES and DMDES precursors used for the synthesis ($n_{\text{MTES}}/n_{\text{DMDES}}$). These numbers need to take into account the relative integrated intensities of carbon signals in $\text{CH}_2\text{-O}$ and $\text{CH}_3\text{-CH}_2\text{-O}$ environments:

$$I_{C,\text{CH}_2-\text{O}} \text{ and } I_{C,\text{CH}_3-\text{CH}_2-\text{O}} .$$

$$n_{C,\text{Me}_2\text{Si}} = I_{C,\text{Me}_2\text{Si}} n_{C,tot} = n_{C,tot} \frac{1 - I_{C,\text{CH}_2-\text{O}} - I_{C,\text{CH}_3-\text{CH}_2-\text{O}}}{1 + 0.5(n_{\text{MTES}}n_{\text{DMDES}})}$$

where the 0.5 comes from there being 2 C atoms per DMDES molecule. Similarly:

$$n_{C,\text{MeSi}} = I_{C,\text{MeSi}} n_{C,tot} = n_{C,tot} \frac{1 - I_{C,\text{CH}_2-\text{O}} - I_{C,\text{CH}_3-\text{CH}_2-\text{O}}}{1 + 2(n_{\text{DMDES}}n_{\text{MTES}})}$$

These numbers impose in turn the number of Si atoms $n_{Si,tot}$, which relates to the relative integrated intensities of Si $T^n$ and $D^n$ species:

$$n_{Si,tot} = n_{Si,tot} \sum_{i=0...3} I_{Si,T^i} + n_{Si,tot} \sum_{i=0...2} I_{Si,D^i} = n_{C,\text{MeSi}} + 0.5n_{C,\text{Me}_2\text{Si}}$$

From there we can compare the number of unreacted Si-O-Et groups, given by:

$$n_{0-\text{CH}_2-\text{CH}_3} = n_{C,tot} I_{C,\text{CH}_3-\text{CH}_2-\text{O}} = n_{C,tot} I_{C,\text{CH}_2-\text{O}}$$

with the number of incompletely-condensed Si sites, i.e. $D^n$ with $n < 2$ and $T^n$ with $n < 3$. (This comparison is simple here because we observe only $D^1$ and $T^2$ sites, meaning that there is no more than one uncondensed O atom per Si):

$$\sum_{i=0...1} n_{Si,D^i} + \sum_{i=0...2} n_{Si,T^i} = \left(n_{C,\text{MeSi}} + 0.5n_{C,\text{Me}_2\text{Si}}\right) \left(\sum_{i=0...3} I_{Si,T^i} + n_{Si,tot} \sum_{i=0...2} I_{Si,D^i}\right)$$

The difference between these numbers should correspond to the number of silanol groups.