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Supporting Information: Glassy Dynamics in Polyalcohols: Inter- vs. Intramolecular Complexity

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I Quantitative analysis of dielectric loss spectra of Xylitol and Sorbitol

In the main manuscript we state that with increasing molecular weight of PAs, the slope β of the high-frequency power law $\omega^{-\beta}$ of the α-process decreases in the dielectric loss spectra. We rationalize this statement in Fig. 1, however it is important to consider that in such a qualitative comparison it is difficult to estimate the influence of the β-process on the high-frequency power law exponent. Therefore, here we perform a quantitative analysis of the peak shapes of Xylitol and Sorbitol. The procedure is as follows: The α-process is modeled using the GG distribution of relaxation times, while the β-process is described by another appropriate distribution presented in Ref. [1]. The combined relaxation function of the two processes is calculated using the William-Watts approach [2] and finally Fourier transformed to the frequency domain to fit the dielectric loss spectra. The respective shape parameters of the distributions of relaxation times are chosen as temperature independent, with the exception of the parameter a of the β-process. The latter is assumed to follow $a \propto T$ which implies an underlying temperature independent distribution of activation energies, which is usually a suitable approximation for the β-process around T_g [1].

The respective fits to the dielectric spectra of xylitol and sorbitol over a broad temperature range are shown in Figure SI. 1. The α-process is well-described by a process with a temperature independent high-frequency slope $\beta = 0.45$ for xylitol and $\beta = 0.37$ for sorbitol.

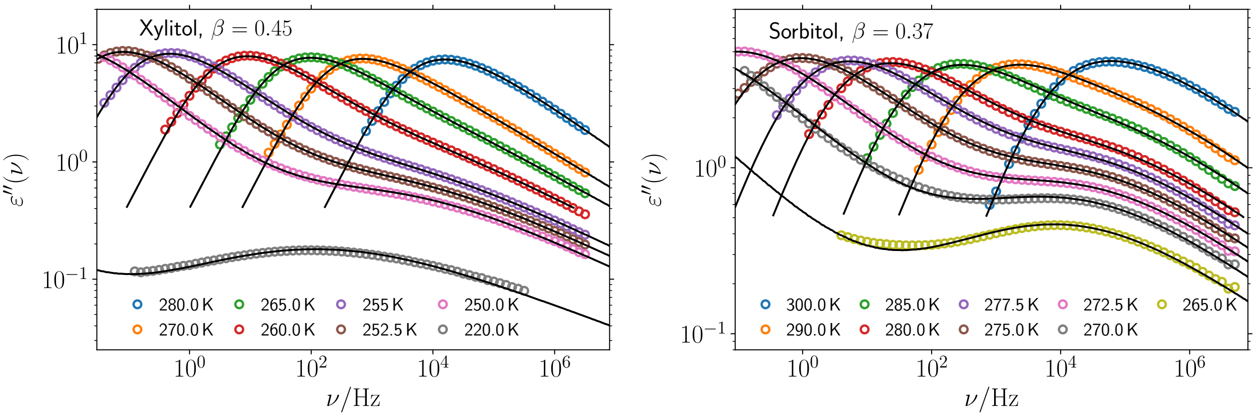

Figure SI. 1: Dielectric loss spectra of xylitol (left) and sorbitol (right) and respective fits to the data using the model described in the text.

II Time-temperature superposition of PCS data

In the qualitative comparison of the different PAs in Fig. 2 we chose the temperatures of the respective PCS spectra to approximately coincide regarding their peak maximum frequencies. However, this condition is in fact not necessary, as time-temperature superposition (TTS) for the α-process holds within the experimental uncertainty. We confirm this in Figure SI. 2, by plotting normalized spectra taken at different temperatures for each PA as a function of $\omega\,\tau_{\mathrm{max}}$. If TTS holds, all spectra should collapse on a single master curve. Indeed, this is observed for all PAs. Only slight deviations can be identified for xylitol and sorbitol at high temperatures. The deviations could result from experimental noise, or due to a weak temperature dependence of the impact of conformational dynamics. The TFPI data suggest that the latter certainly should be observable over a broad temperature range, however it is unclear whether these effects are already resolved in the temperature range accessible by PCS.

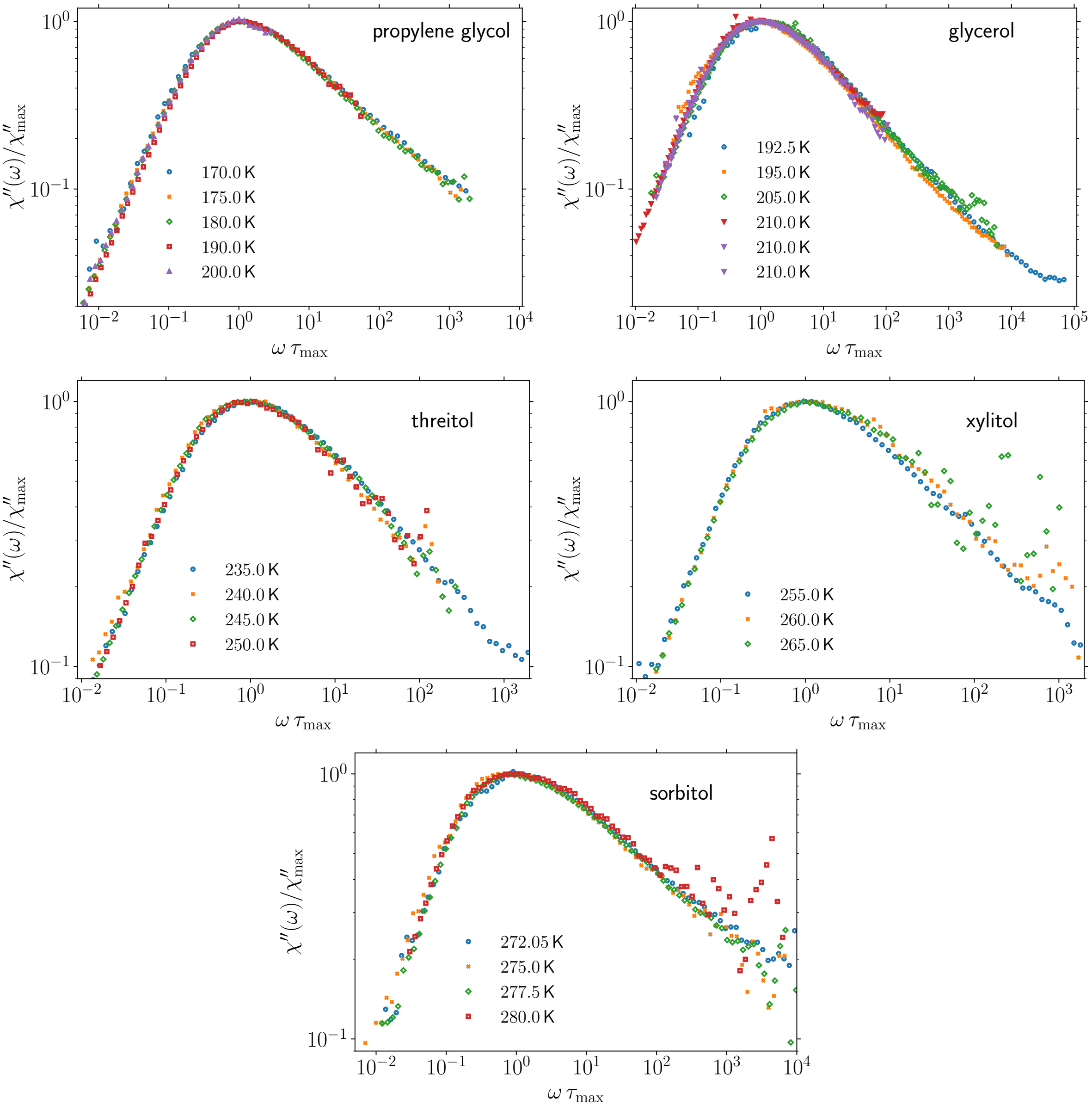

Figure SI. 2: Master curves of the normalized PCS spectra as a function of $\omega\,\tau_{\mathrm{max}}$ to verify TTS.

III Combined PCS and BDS analysis for propylene glycol

In Fig. 4 of the main manuscript we present PCS and BDS data for propylene glycol (PG). We state in the text that the results for PG and glycerol are qualitatively comparable regarding separation of the peak maxima and difference between high-frequency power law exponent of both techniques. For glycerol, these aspects were discussed extensively in Ref. [3]. To support our claims we now present the analysis for PG. In Figure SI. 3 (left), BDS and PCS data for a broad range of temperatures are shown. We fit the PCS data, using a temperature independent distribution of relaxation times for the α-process and a temperature independent distribution of activation energies for the β-process, both are specified in Ref. [1]. The combined relaxation function of the two processes is calculated using the Williams–Watts approach [2] and finally Fourier transformed to the frequency domain. BDS data are fitted using the expression:

$$\phi_{\mathrm{BDS}}(t) = \Delta\varepsilon_{\mathrm{cross}} \cdot \exp\left[-\left(\frac{t}{\tau_{\mathrm{cross}}}\right)^{\beta_{\mathrm{cross}}}\right] + \Delta\varepsilon_{\alpha\beta} \cdot \phi_{\mathrm{PCS}}(t), \tag{1}$$

again Fourier transformed to the frequency domain. This approach is based on the assumption, that the PCS spectra represent the self-part of molecular dynamics, which in BDS is superimposed by slow cross-correlation contributions. Due to being significantly slower than the α-process, cross-correlations follow a close-to exponential shape. For PG the analysis yields values of $0.86 < \beta_{\mathrm{cross}} < 0.92$, which are slightly larger than the ones obtained for glycerol [3]. In Figure SI. 3 (right) we show the peak relaxation times τ_{cross} and τ_α of cross-correlations and the α-process, respectively. Both are separated by a factor $10 < \tau_{\mathrm{cross}}/\tau_\alpha < 20$ depending on the temperature, as shown in the inset.

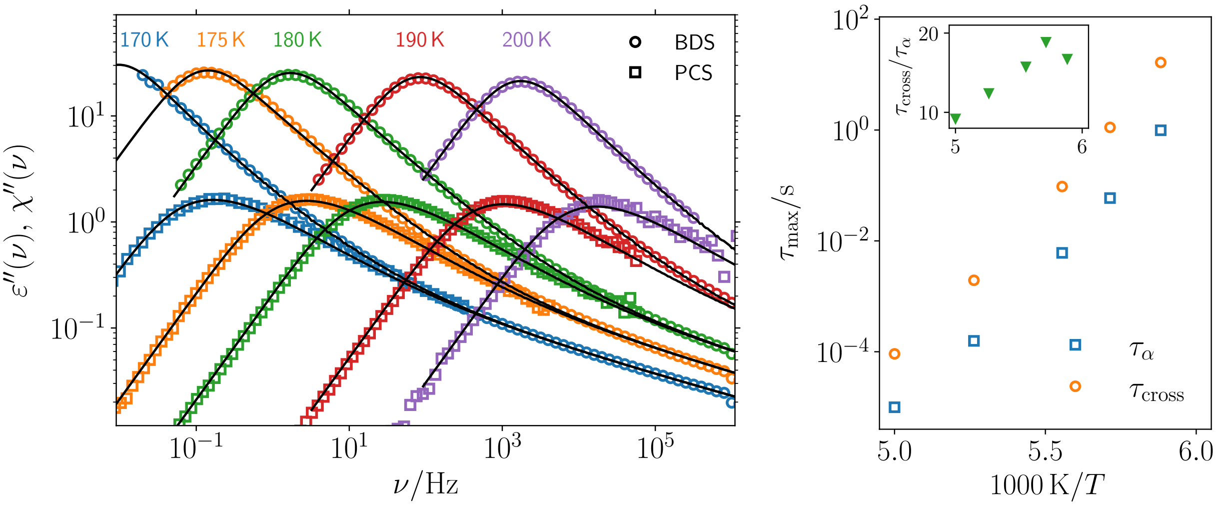

Figure SI. 3: Left side: PCS and BDS data of PG at the indicated temperatures and respective fits, calculated using the procedure explained in the text. Right side: Temperature dependence of the peak relaxation times of cross-correlations and of the α-process. The quotient $\tau_{\mathrm{cross}}/\tau_\alpha$ is shown in the inset.

IV ^{13}C-NMR relaxation times for Sorbitol

In Fig. 4 of the main manuscipt we present site-resolved time constants from ^{13}C-NMR of different C-H bonds in the molecule. The time constants extracted from Ref. [4] are shown in Figure SI. 4. To compare them to our DLS spectra, we fit the NMR time constants using the Arrhenius equation (black lines) and extrapolate to $T = 420\,\mathrm{K}$ (red symbols), which is the temperature studied in DLS.

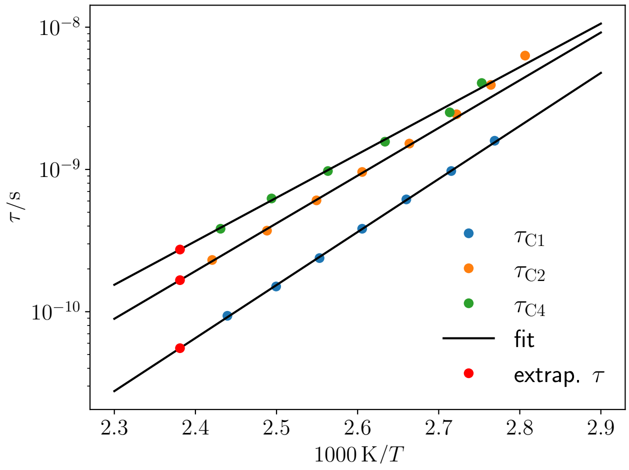

Figure SI. 4: Site-resolved time constants from ^{13}C-NMR of different C-H bonds from Ref. [4] (symbols), fitted by the Arrhenius equation and extrapolated to $T = 420\,\mathrm{K}$ (red symbols).

References

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