

# Dynamics of Poly(vinyl butyral) studied by Dielectric Spectroscopy and <sup>1</sup>H NMR Relaxometry

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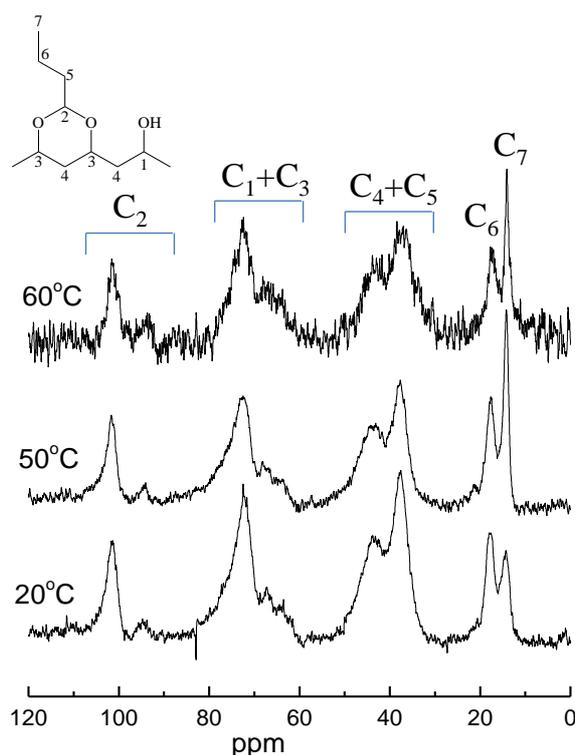
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## S1. $^{13}\text{C}$ CP MAS NMR Spectroscopy

### Experimental

$^{13}\text{C}$  Cross Polarization Magic Angle Spinning (CP MAS) spectra were acquired on a Bruker AMX-300 WB spectrometer equipped with a 4 mm probe. The operating frequencies were 300.13 and 75.47 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively. Standard sequences were applied in order to measure the  $^1\text{H}$   $T_1$  relaxation times at a Larmor frequency of 300 MHz with acquisition on the  $^{13}\text{C}$  channel *via* CP in the temperature range 20-60 °C. The 90° pulse duration was 3.9  $\mu\text{s}$  on the  $^1\text{H}$  channel. The MAS speed was set to 8 kHz, the decoupling field strength in frequency units,  $\nu_{1H}$ , to 64 kHz, the contact time to 1 ms, and the recycle delay to 7 s. The experiments were performed on heating and letting the sample equilibrate for 10 minutes before each measurement. The temperature was controlled within  $\pm 0.1$  °C with a BVT 1000 (Eurotherm) variable temperature unit. Air was used as heating gas.

### Results and discussion



**Figure S1.**  $^{13}\text{C}$  CP MAS spectra of PVB acquired at different temperatures. One should notice that no signal is detected at about 58 ppm, the chemical shift characterizing the methylene carbon in ethanol, this ruling out the presence of residual ethanol in a constrained environment.

$^{13}\text{C}$  CP MAS spectra acquired on the PVB film in the 20-60 °C temperature range are shown in Figure S1 together with signal assignment based on ref. 1. Above 60 °C the CP was not effective, due to the decrease of the  $^{13}\text{C}$ - $^1\text{H}$  dipolar interaction in the proximity of the glass transition, which is responsible for the reduction of the signal/noise ratio already observable at 60 °C.

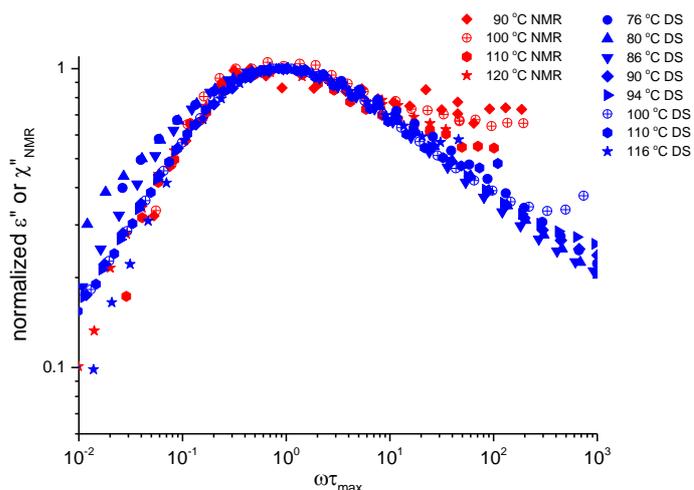
By exploiting the resolution of  $^{13}\text{C}$  CP MAS spectra, we measured  $^1\text{H}$   $T_1$  for the functional groups that can be distinguished in the spectra at a Larmor frequency of 300 MHz in the 20-60 °C temperature range. A single  $^1\text{H}$   $T_1$  value, common to all groups, was determined at each investigated temperature, indicating that spin diffusion is effective. A single  $T_1$  value was observed also in different types of poly(vinyl formal) and attributed to spin diffusion.<sup>2</sup> Furthermore, the  $^1\text{H}$   $T_1$  values found at different temperatures were all equal to  $1.3 \pm 0.1$  s within the experimental error. These data, together with those obtained by  $^1\text{H}$  Free Induction Decay analyses in a parallel study,<sup>3</sup> indicate that the methyl rotation about its ternary axis has frequencies higher than 300 MHz at the investigated temperatures, as expected.<sup>4</sup>

Further information on the dynamics of the different polymer groups could be inferred from the trends of the peak linewidths as a function of temperature in the  $^{13}\text{C}$  CP MAS spectra. In fact, the linewidth of the peak due to the methyl carbon decreased from 150 to 90 Hz upon heating from 20 to 50 °C, whereas the linewidth of the other signals did not change significantly (in Figure S1). Line broadening may arise from chemical shift dispersions, due to different conformations and variation in local susceptibility, and from relaxation processes, such as motional modulation of the chemical shift anisotropy and of the dipolar carbon-proton coupling. No different conformations were observed for the methyl carbons in solution<sup>5</sup> and the methyl line shape here observed is quite symmetric. Moreover, considering the principal values of the chemical shift tensor for the methyl carbon in eicosane,<sup>6</sup> at the applied field (7 T) and spinning rate value ( $\nu_{\text{rot}}=8$  kHz) we estimate that the broadening due to the motional modulation of the chemical shift anisotropy is at most 28 Hz, when the correlation time is equal to  $1/(2\pi \cdot \nu_{\text{rot}})$ , that is on the order of 20  $\mu\text{s}$ .<sup>7</sup> However, based on the  $T_1$  data at 300 MHz, the correlation time and, therefore, the broadening due to this mechanism is actually much lower. On the other hand, the motional modulation of the dipolar C-H coupling is expected to give much larger broadening.<sup>7</sup> By assuming this mechanism for line broadening and considering that the methyl linewidth,  $\Delta\nu$ , decreases upon heating and the methyl motional rate is larger than  $^1\text{H}$  decoupling field strength in frequency units,  $\nu_{1\text{H}}$ , we inferred that  $\Delta\nu$  is proportional to the correlation time,  $\tau$ , and we exploited this relationship to estimate the activation energy,  $E_{\text{act}}$ , for the methyl rotation. Assuming that the correlation time is characterized by an Arrhenius temperature dependence,  $\tau(T) = \tau_{\infty} e^{E_{\text{act}}/RT}$ , from  $\Delta\nu$  values at 20 and 50 °C we found  $E_{\text{act}}=3.3 \pm$

0.1 kcal/mol, which is close to a value previously reported for methyl rotation in PVB ( $2.7 \pm 0.2$  kcal/mol).<sup>8</sup>

The absence of linewidth changes for the other signals can be accounted for by considering that in the glassy state between 20 and 50 °C the motional frequencies of the other groups are much lower than  $\nu_{1H}$ .<sup>3</sup>

## S2. Frequency Temperature Superposition of DS and FFC NMR data



**Figure S2.** Frequency Temperature Superposition for  $\varepsilon''$  and  $\chi''_{\text{NMR}}$  data at the indicated temperatures. Curves at different temperatures were normalized dividing by the maximum amplitude value.

Figure S2 compares the  $\varepsilon''$  and  $\chi''_{\text{NMR}}$  curves acquired above  $T_g$  after scaling the amplitude and the time scale. It can be observed that the two series of curve differ on both sides of the maximum.  $\chi''_{\text{NMR}}$  curves at 70 and 80 °C could not be included in the figure with the same scaling procedure because no maximum is evident for the  $\alpha$  process in those curves.

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