

Dynamics of di(propylene glycol) dibenzoate-d₁₀ in poly(vinyl acetate) by solid state ²H NMR

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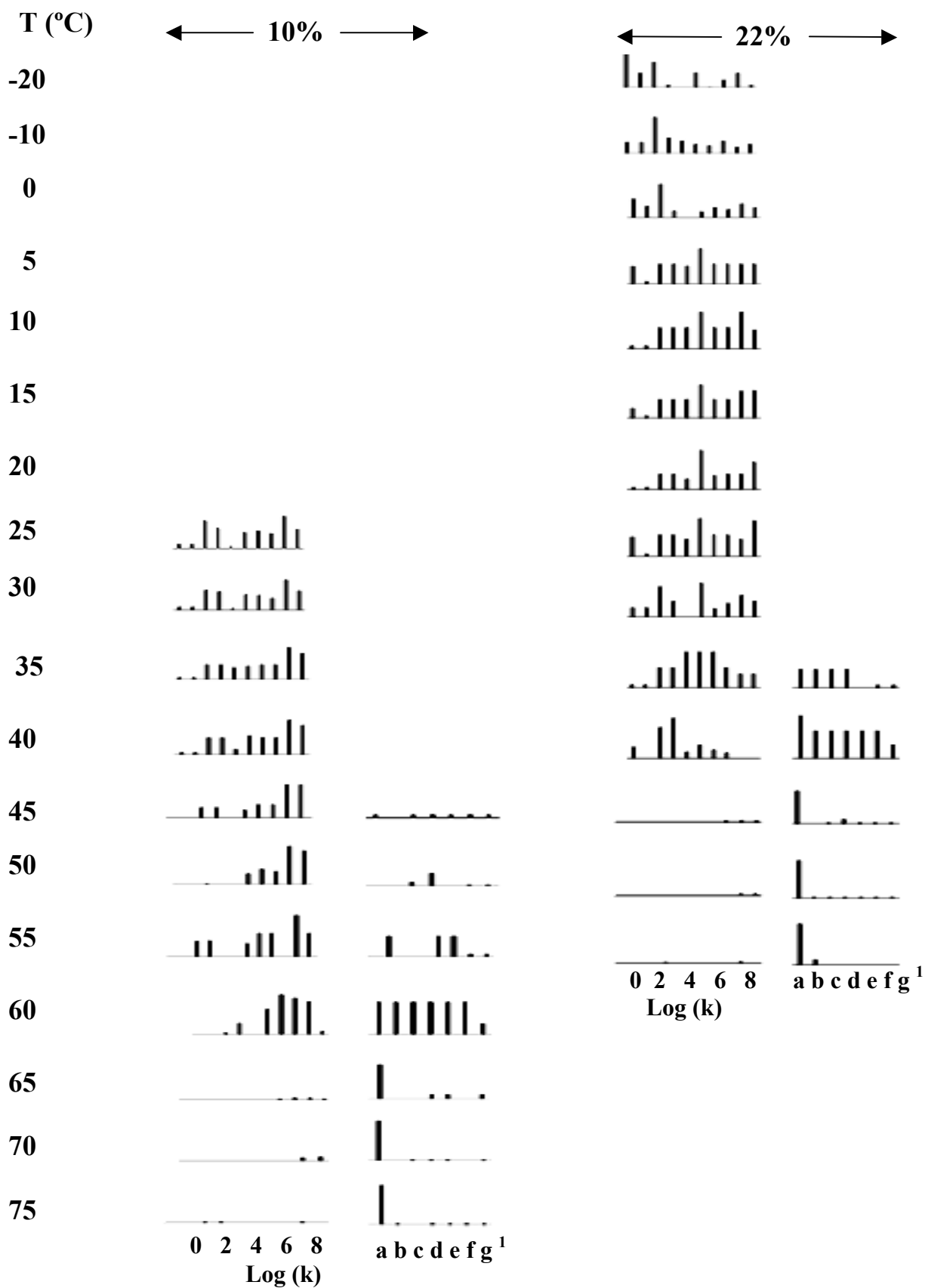
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SUPPORTING INFORMATION

S1. Fitting Components Used in the Deuterium NMR Spectra

The phenyl ring motions were categorized into three groups or regimes with respect to their jump rate (k); as slow ($k < 1 \times 10^4$ Hz), intermediate ($1 \times 10^4 < k < 1 \times 10^8$), and fast ($k > 1 \times 10^8$) which have in different powder pattern intensities. As shown in scheme D1, slow motions yielded a rigid powder pattern. While the intermediate motions showed simultaneous changes in the ^2H NMR line shapes with a significant loss of intensity. In the fast motion regime, the quadrupole splitting was reduced and if the motion was fast enough, it was eliminated indicating that an additional motion was occurring. The *para* deuterons were not affected by a 180° jump about the 1,4 phenylene flip axis because this rotation did not change the orientation of that C-D bond; only a small amount of intensity loss occurred. A 180° jump about the C_2 symmetry axis would not yield an isotropic motion, even with the fast exchange rate, $k > 10^8$. The addition of another of motion was needed to further average the qcc to obtain an isotropic pattern (a narrow single peak). For this work, it was sufficient to add a Gaussian single central component.

The experimental line shapes were then fitted using a mathematical routine (MATLAB, the Mathworks, Inc., Natick, MA). The distributions of jump rates from the simulations for bulk PVAc samples with 10, 22, 27, and 37% w/w plasticizer/PVAc at various temperatures are shown in Figure S1.



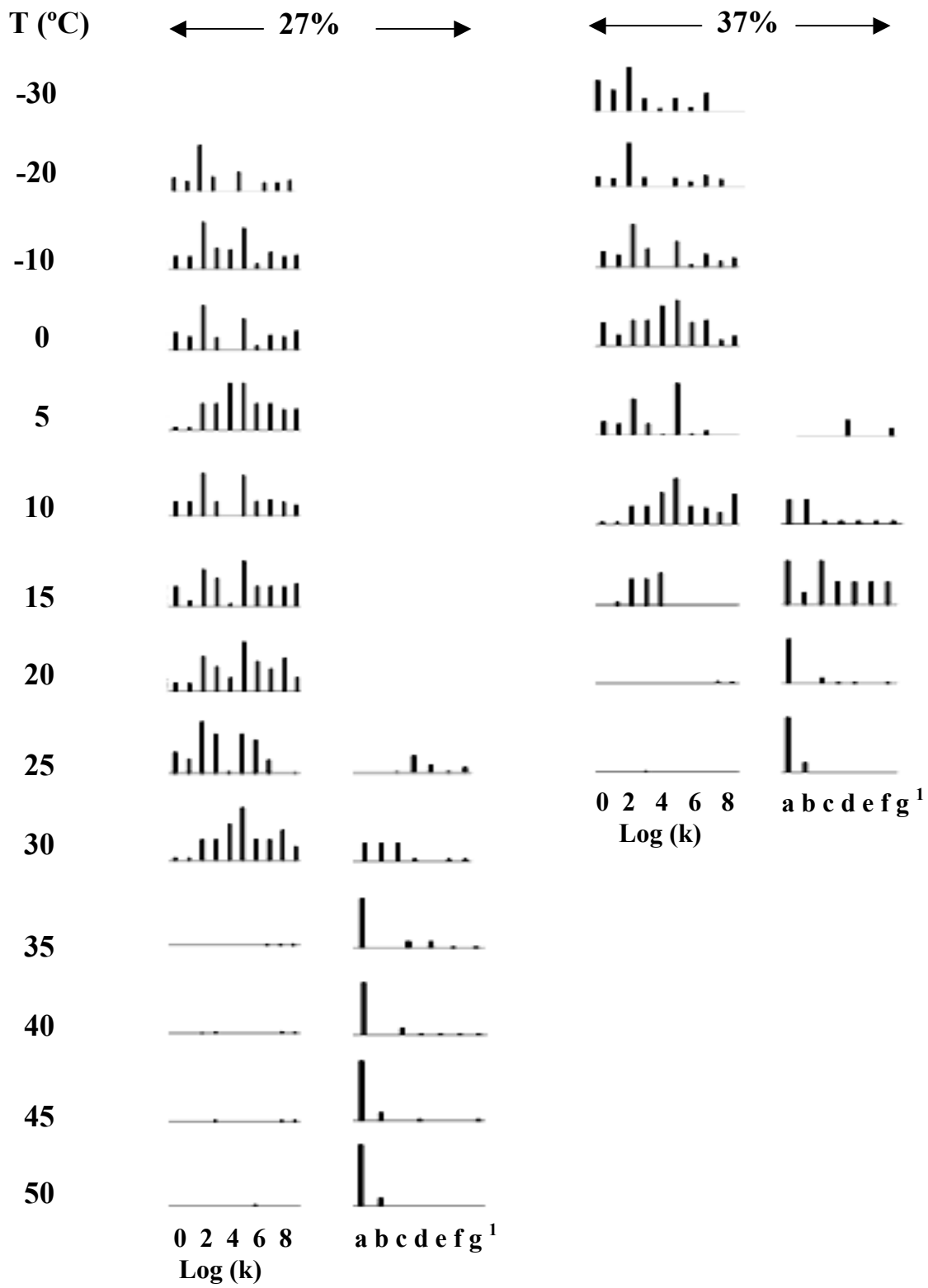


Figure S1. Distributions of jump rates from the simulations for each of the experimental spectra for the DPGDB-d₁₀ in PVAc samples with 10, 22, 27, and 37% w/w plasticizer/PVAc at various temperatures. Slow, intermediate, and fast motions are represented by the log of jump rate (log k) from 0-9. ¹The liquid like component is represented by the letters a-g indicating jump rate independent for a change in NMR line shapes. The line widths for the isotropic resonances (letters a-g) are given in Table S1.

Table S1. Assignments for the Liquid Like Components of the Simulations

Assigned letter	Quadrupole coupling constant (QCC) (kHz)	Gaussian Broadening (GB) (kHz)	Lorentzian Broadening (LB) (kHz)
a	1	5	5
b	5	1	1
c	5	5	5
d	5	10	10
e	5	20	20
f	5	0	5
g	5	0	10
h	5	0	20
i	1	1	1
j	1	0	1
k	1	0	5

S2. Fitting Components Used in the Deuterium NMR Spectra

The log of the average jump rates (log $\langle k \rangle$) as a function of temperature for different plasticizer contents (10, 22, 27, and 37%) are shown in Figure S3. The plot of log $\langle k \rangle$ values, as a function of inverse temperature for different plasticizer contents seemed to be linear for small amounts of plasticizer (10-22%). As the amount of plasticizer increased, the deviation from linearity was more pronounced. The activation energies for the 180° ring flips from linear portions for both the 10 and 22% plasticizer content were calculated to be 25 kJ/mol. However, as stated in the main text, the use of $\langle \log k \rangle$ is perhaps more indicative of the behavior of the plasticizer as there are contributions very different time scales.

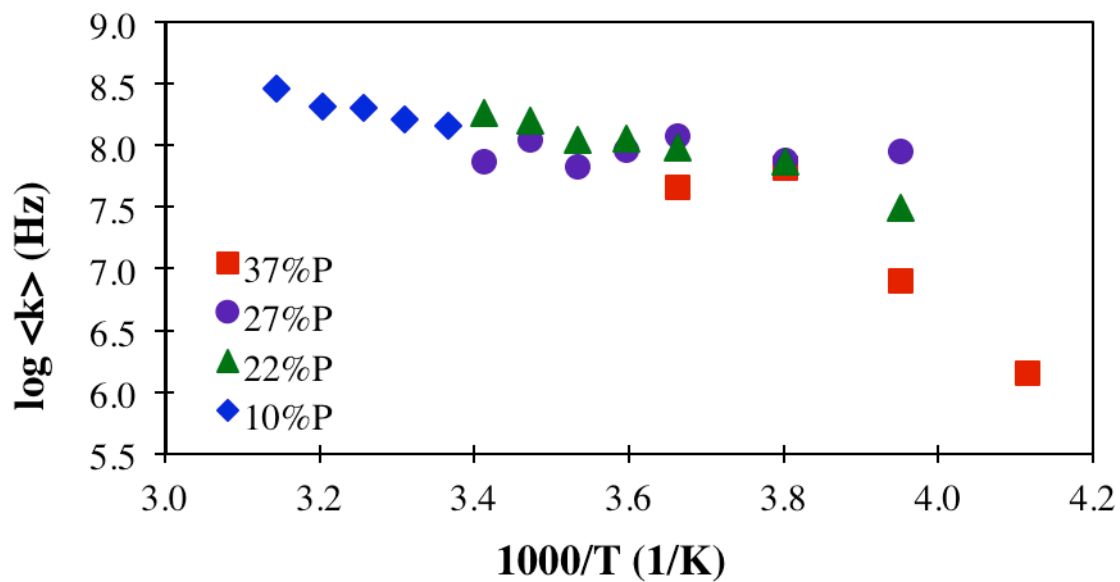


Figure S2. The log average jump rates values ($\log \langle k \rangle$) for DPGDB-d₁₀ as a function of temperature for the different plasticizer contents (10, 22, 27, and 37%).