

# Dielectric and Shear Mechanical Spectra of Propanols: The Influence of Hydrogen-Bonded Structures

Mathias Mikkelsen, Jan Philipp Gabriel, and Tina Hecksher\*



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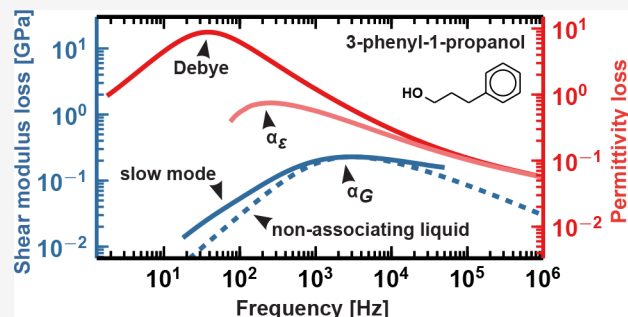


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**ABSTRACT:** We present a dielectric and shear mechanical study of 1-propanol and three phenylpropanols. Contrary to other monoalcohols, the phenylpropanols do not show a bimodal behavior in their dielectric response, but instead show a single, rather narrow process. Combined dielectric and light scattering spectra (Böhmer, T.; et al. *J. Phys. Chem. B* 2019, 123, 10959) have shown that this single peak may be separated into a self- and a cross-correlation part, thus indicating that phenylpropanols do display features originating from hydrogen-bonded structures. The shear mechanical spectra support that interpretation, demonstrating a subtle, yet clear, low-frequency polymer-like mode, similar to what is found in other monoalcohols. An analysis of the characteristic time scales found in the spectra shows that shear alpha relaxation is faster than the dielectric alpha and alpha processes is temperature independent and nearly identical in all the phenylpropanols.



## INTRODUCTION

Monoalcohols continue to attract attention due to their intriguing anomalous dielectric response.<sup>2,3</sup> Many monoalcohols display an intense, single-exponential peak, in contrast to the asymmetric relaxation shape corresponding to a broad distribution of relaxation times dominant in most supercooled neat systems. The process is not correlated with the calorimetric glass transition,<sup>4–6</sup> which instead seems to be related to the high-frequency shoulder in the dielectric spectrum. The latter process is therefore identified as the structural alpha relaxation, while the first is nowadays referred to as the Debye process due to its often single-exponential shape. In general, the intensity of the Debye process varies greatly with the molecular architecture; sometimes having a similar intensity to the alpha process, e.g., in 4-methyl-3-heptanol,<sup>7–10</sup> or even lower, e.g., in 3-methyl-3-heptanol.<sup>8,10</sup> In pure monoalcohols, the temporal separation between the Debye and alpha processes correlates with the relative intensity: the greater the temporal separation between the Debye and alpha processes, the larger the Debye intensity.<sup>11</sup>

Since the 1950s, the general consensus regarding the Debye process is that it originates from transient supramolecular structures formed by hydrogen bonds.<sup>7,12–14</sup> Since monoalcohols only have one OH-group per molecule, primarily linear structures are formed which can have a large end-to-end dipole moment (chains) or nearly zero dipole moment (rings).<sup>15</sup> The (distribution of) specific structures formed thus result in different dielectric strengths that can vary with temperature,<sup>16</sup> can be tweaked by mixing,<sup>17–19</sup> and has been shown to also be sensitive to a DC bias field.<sup>20,21</sup> The relaxation mechanism of these hydrogen-bonded clusters is not well understood, most

notably why only one time scale is necessary to describe their relaxation.

The Debye process in monoalcohols was initially believed to be a purely dielectric phenomenon.<sup>22</sup> This is likely rooted in the difficulty of resolving the contribution in techniques where the effect is not as pronounced as in the dielectric probe. Later, a subtle yet consistent signature of a Debye process in the dynamic shear modulus similar to that of a short-chain polymer was discovered.<sup>10,23</sup> This finding was further confirmed by other rheological techniques and in more systems.<sup>10,24–28</sup>

Recently, the presence of a process slower than the alpha was demonstrated in the light scattering spectrum of 5-methyl-2-hexanol.<sup>29</sup> This slow process has approximately the same temperature dependence as the dielectric Debye process and merges with the alpha relaxation at high and low temperatures. The intensity of the slow process relative to the alpha process is, on the other hand, orders of magnitude lower than in dielectrics. This is likely due to the fact that depolarized light scattering probes the self-part of the rotational correlation function, while the dielectric response measures the macroscopic dipole moment coming from both individual dipoles and cross-correlations. The slow process is thus a “spillover” effect of the

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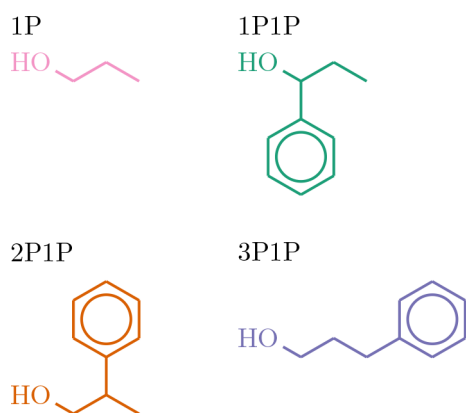
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cross-correlations: the supramolecular structure hinders the total orientational decorrelation of individual molecules, that then only fully relax when the supramolecular structure has relaxed. The finding of a low-frequency (Debye) process in the light scattering spectrum is *not* general. In some monoalcohols, it is absent (or not resolvable).<sup>30,31</sup>

Further works comparing depolarized light scattering to dielectric spectra have shown that the two techniques in combination may be used to separate the self and cross parts of the rotational correlation function in other associating—and even nonassociating—polar liquids.<sup>32,33</sup> This is also the case when there is not a clearly bimodal dielectric spectrum, e.g., in glycerol.<sup>34</sup>

The present paper investigates a series of propanols (see Figure 1) previously investigated with dielectric spectroscopy



**Figure 1.** Structure of the measured compounds: 1-propanol (1P), 1-phenyl-1-propanol (1P1P), 2-phenyl-1-propanol (2P1P), and 3-phenyl-1-propanol (3P1P). 1P1P and 2P2P have chiral centers (at the first and second carbon atoms of the propane chain, respectively).

and light scattering<sup>1</sup> and—in the case of 1-phenyl-propanol—high-field dielectric spectroscopy.<sup>21</sup> Böhmer et al.<sup>1</sup> showed that the phenylpropanols are not as sterically prevented from forming hydrogen-bonded structures as previously assumed.<sup>35</sup> The analysis of combined light scattering and dielectric spectra reveals that the single dielectric peak can be interpreted as a merging of a Debye and  $\alpha$ -relaxation.

Shear mechanical spectroscopy in combination with other techniques has proven to be a useful tool to discern different processes in monoalcohols and other associating liquids,<sup>36</sup> and thus, shear mechanical measurements of this series of propanols will shed more light on the interpretation of the combined dielectric and light scattering spectroscopy. In this work we present shear mechanical and dielectric spectra of 1-propanol and phenylpropanols obtained under identical experimental conditions and compare spectral features and characteristic time scales extracted from the measurements.

## EXPERIMENTAL DETAILS

The investigated substances are *x*-phenyl-1-propanol with *x* = 1, 2, 3 which is 1-propanol with a phenyl ring on position 1, 2, and 3, respectively, in the alkyl chain. Previously published data<sup>37</sup> for 1-propanol (1P) are included for comparison. The chemical structures of the propanols are shown in Figure 1. 1-Phenyl-1-propanol (1P1P) was purchased from Alfa Aesar, and 2-phenyl-1-propanol and 3-phenyl-1-propanol (2P1P, 3P1P) from TCI (see Supporting Information). All samples were stored and

loaded into sample cells under a dry atmosphere in a glovebox and used with no further purification.

The dynamic shear modulus was measured over more than seven decades of frequency (1 mHz to 50 kHz) with the piezoelectric shear gauge method.<sup>38–40</sup> Compared to conventional rheometers, this technique is optimized for measurements on stiff systems (1 MPa to 10 GPa)<sup>38</sup> and thus is well-suited for liquids studied close to their glass transition temperature. In addition, dielectric measurements with a parallel plate capacitor were performed in the same custom-built cryostat system.<sup>41,42</sup> This ensured that shear and dielectric data sets were measured under identical experimental conditions. In particular, absolute temperatures were the same in the two measurements and direct comparisons between methods may be made.

## RESULTS

Figure 2 shows the complex dielectric permittivity (top panel) and the complex shear modulus (bottom panel) of 1-propanol and the phenylpropanols. The dielectric data are in qualitative and quantitative agreement with previously published data.<sup>1</sup> The dielectric strength gradually decreases from  $\Delta\epsilon \sim 40$  in 1-propanol, to around  $\Delta\epsilon \sim 10$  in 1P1P. We interpret this to be a sign of the phenyl ring sterically hindering the formation of chain-like structures, which would have a large end-to-end dipole moment.

The shear mechanical spectra for the three phenylpropanols are on the other hand quite comparable in strength, i.e., high-frequency plateau modulus  $G_\infty \sim 1\text{--}2$  GPa, and shape, only deviating in the onset of a secondary relaxation toward the high-frequency end of our frequency window. The shear spectra of 1-propanol have similar  $G_\infty$  values but stand out due to an intense secondary relaxation rather low in frequency.

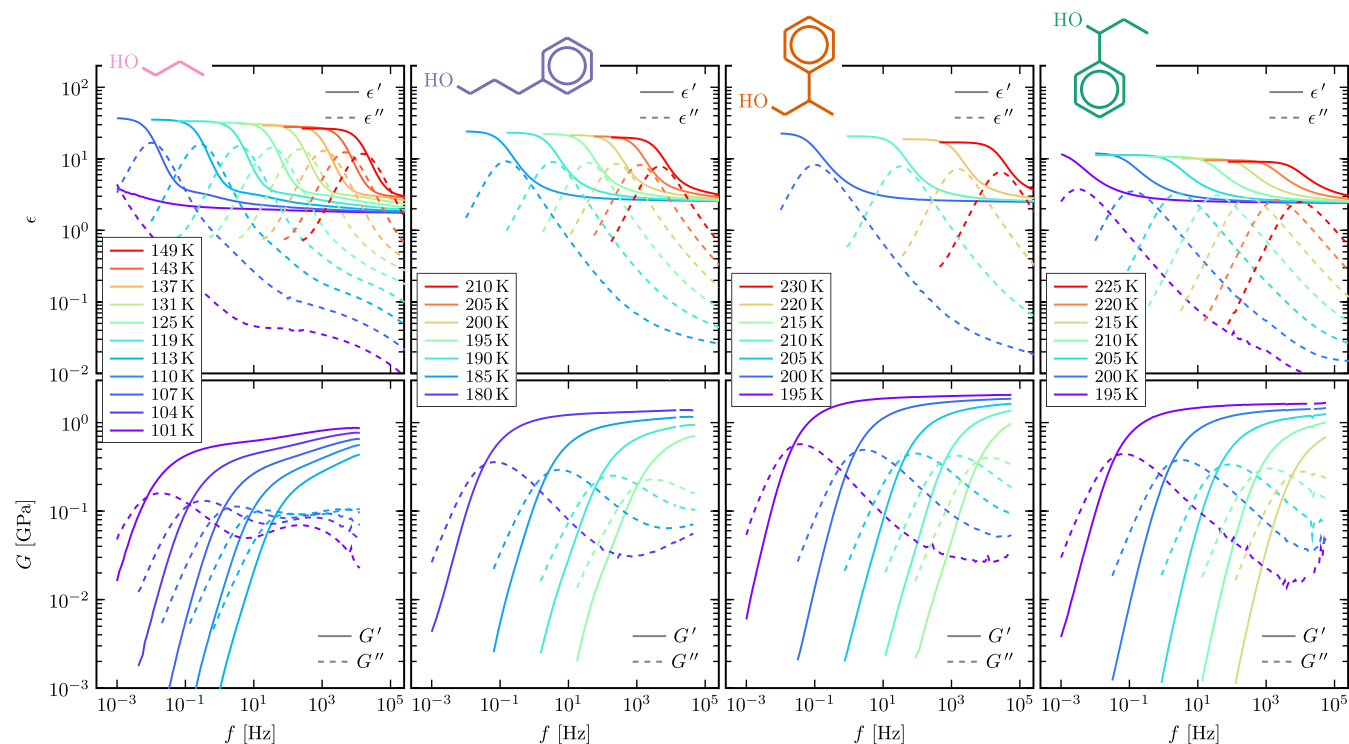
At first glance no obvious low-frequency, polymer-like behavior is visible in any of the shear mechanical spectra. At low frequencies, all spectra seem to terminate with the final power laws of  $\omega^1$  for  $G'$  and  $\omega^2$  for  $G''$  as expected for a purely viscous flow.

For a closer look on the low-frequency part of the spectra, Figure 3 shows dielectric and shear mechanical spectra at selected temperatures (one high and one low) scaled on the frequency axis by the shear loss peak frequency. For comparison, a prototypical monoalcohol, 2-ethyl-1-hexanol (2E1H) (data from ref 36), and a prototypical simple glass former, tetramethyl tetraphenyl trisiloxane (DC704) (data from ref 40), are also added.

Figure 3a shows the imaginary part of the dielectric spectrum for each substance. The permittivity axis has not been scaled, but since the frequency axis is now scaled by the shear loss peak frequency, the differences in intensities and in separation between the Debye and alpha peaks become clear. The peak value of  $\epsilon''$  for 2P1P and 3P1P is higher than for 1P1P, while the peak positions are nearly the same. The Debye peak of 1P is even more intense and shifted to lower frequencies. Interestingly, the high-frequency flanks representing the alpha relaxation are a factor of 10 higher in 1P and all phenylpropanols than in 2E1H.

The low alpha intensity seen in many monoalcohols is interpreted to stem from the fact that part of the molecular dipole moment is locked in hydrogen-bonded structures, and thus, the part left for the alpha relaxation is diminished.<sup>2</sup>

In Figures 3(b, c), the real and imaginary parts of the shear modulus—both scaled with the loss peak value—are shown. Plotted like this, it is clear that there is a slight broadening on the low-frequency side of 1-propanol and the phenylpropanols



**Figure 2.** Dielectric (top panel) and shear mechanical (bottom panel) spectra for 1-propanol and the three phenylpropanols. 1P data have previously been published.<sup>37</sup> All sets of shear mechanical and dielectric data have been measured on the same bottle and in the same cryostat system ensuring identical experimental condition and thus allowing a direct comparison. Data are available at <http://glass.ruc.dk/data/>.

compared to DC704; however, nothing like the pronounced shoulder found in 2E1H.

Figure 3(d) shows the logarithmic derivative of the imaginary part,  $\frac{d \log(G'')}{d \log(f)}$ . This quantity is zero at the peak and approaches a constant above and below the peak if there is a limiting power-law behavior in the data. In particular, it should approach 1 at low frequencies, signaling the onset of purely viscous flow expected for a liquid. For the reference liquid DC704 (blue dashed line), the curve increases monotonously and approaches 1 going down in frequency from the loss peak. For 2E1H (green plusses), there is a clear two-step behavior, where the curve levels off at  $\sim 2/3$  for roughly two decades before rising to the expected value of 1.

This plot reveals that the phenylpropanols and the 1-propanol fall in between these two cases. 2P1P (orange squares) and 3P1P (purple diamonds) clearly display a two-step behavior, albeit with a shorter frequency span than 2E1H. However, this two-step behavior gradually disappears with decreasing temperature (see Supporting Information for more details). It is replaced by a less steep transition to the limiting viscous behavior than that of DC704, which corresponds to the phenylpropanols having broader loss peaks. 1P1P (green circles) shows this characteristic broadening independent of temperature and never a two-step behavior.

Characteristic time scales from the spectra are presented in Figure 4. All time scales are obtained as loss peak frequencies: The shear mechanical loss peak is found by fitting a few points around the maximum of the imaginary part,  $G''$ , to a second order polynomial, and the dielectric Debye peak is determined in the same way—as the frequency of the peak in the dielectric loss. The dielectric alpha peak is determined assuming additivity of Debye and alpha relaxations and subtracting from the

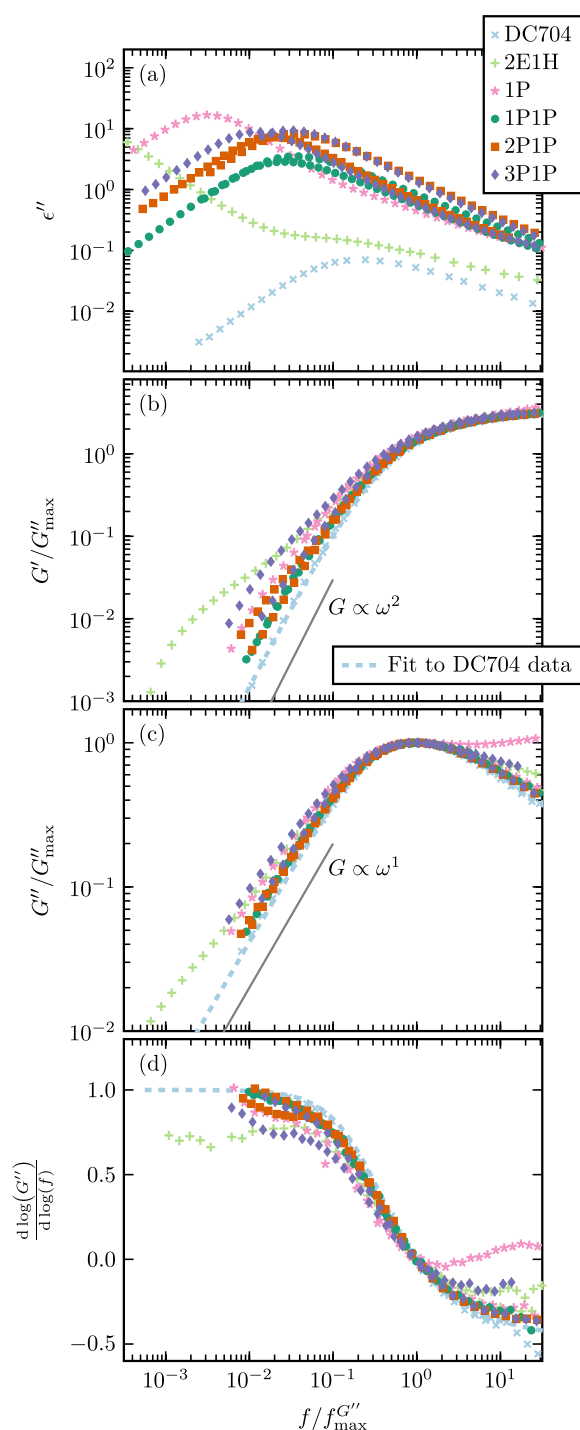
spectrum a purely exponential relaxation (fitted to the low-frequency side of the Debye peak). The peak of the remaining spectrum is then assumed to be the alpha peak (see Supporting Information for more details).

Figure 4(a) shows the obtained loss peak frequencies as a function of inverse temperature. 1P1P and 2P1P have identical peak positions and temperature behavior for all three time scales and thus have identical glass transition temperatures, whereas the time scales of the more elongated 3P1P molecule are at lower temperatures, i.e., relaxation at a given temperature is faster in 3P1P.

Figure 4(b, c) shows the time scale index<sup>44,45</sup> (this is sometimes referred to as a “decoupling index”) plotted as a function of the dielectric alpha loss peak frequency instead of temperature. Plotted this way, all substances share a common axis, namely the measurement frequency window. The time scale index is defined as the logarithm of the ratio of two time scales

$$I_x = \log_{10}(f_{\max}^x / f_{\max}^\alpha) \quad (1)$$

where  $f_{\max}^\alpha$  is the dielectric alpha loss peak which is chosen as the reference time scale, while  $f_{\max}^x$  is the loss peak of another process/quantity,  $x$ . Again, the reference liquids DC704 and 2E1H are added for comparison. The first thing to notice is that the shear alpha time scale is consistently faster than the dielectric alpha time scale by roughly a factor of 10. This is in line with previous observations for both associating and van der Waals type molecular liquids.<sup>44–46</sup> There is a significant spread in the exact factor of separation, but for most substances it is nearly temperature independent. Even more striking is the fact that the Debye and alpha separation in all the phenylpropanols is identical and temperature independent—except toward the highest temperatures (higher loss peak frequencies), where the



**Figure 3.** Selected shear mechanical and dielectric spectra as a function of frequency scaled to the peak position of the shear loss peak of 1P, 3P1P, 2P1P, and 1P1P in a comparison with standard glass former DC704 and prototypical monoalcohol 2E1H. (a) Dielectric data. (b, c) Real and imaginary parts of the shear modulus scaled by the shear loss peak maximum value. (d) The logarithmic derivative of  $G''$ . Literature data are taken from Gainaru et al.<sup>25</sup> and Jakobsen et al.<sup>43</sup> for 2E1H and from Weigl et al.<sup>37</sup> for 1P. DC704 data are from Mikkelsen et al.<sup>40</sup>

separation seems to increase (the index tends toward lower values) in 3P1P. This indicates that in the phenylpropanols there is no decoupling between Debye and alpha time scales and thus apparently no temperature where the two processes merge. In fact, in 3P1P the two processes seem to separate more as

temperature increases. As was already evident in Figure 3(a) the separation between Debye and alpha is larger in 1P (roughly a factor 100) and even larger in 2E1H (roughly a factor 1000).

## DISCUSSION AND CONCLUDING REMARKS

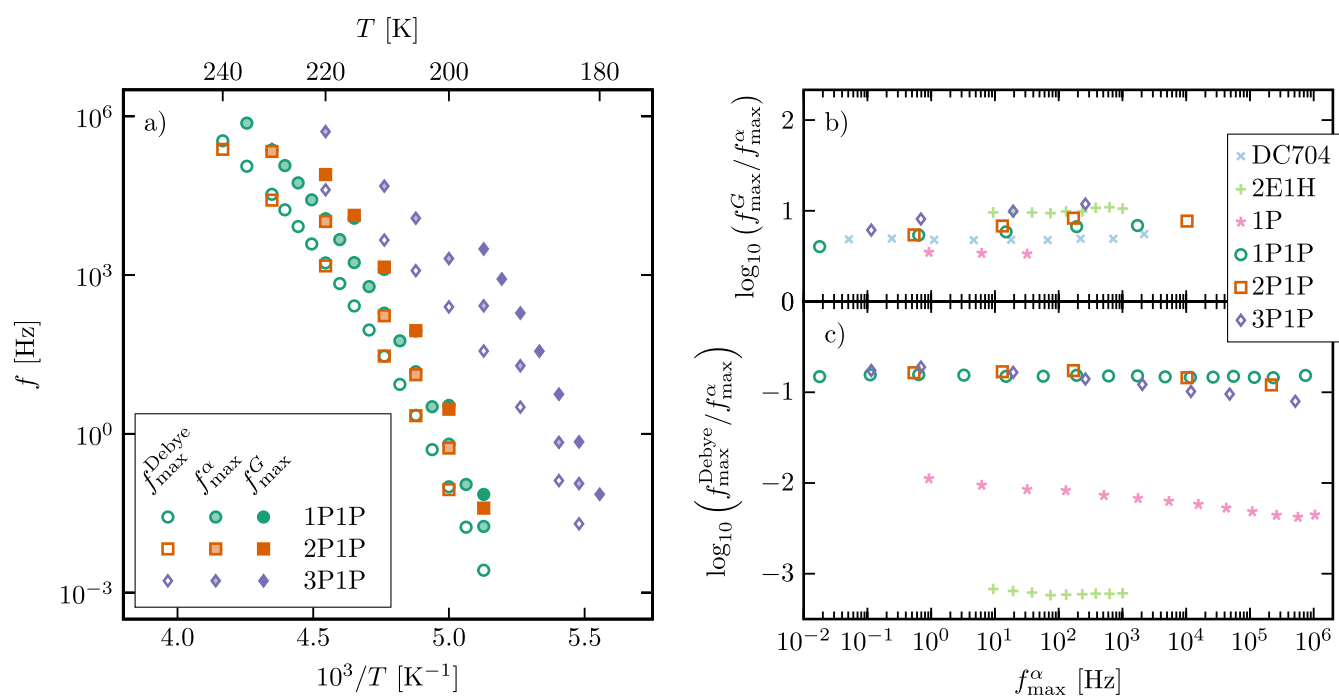
Böhmer et al.<sup>1</sup> suggested that the dielectric spectra of the phenylpropanols—just like other monoalcohols—are dominated by the cross-correlation between molecules. The cross-correlations are presumably mainly due to hydrogen-bonded structures, despite the fact that the spectrum is displaying only a single asymmetric peak. The present results support that interpretation, as the mechanical spectra show a subtle yet distinct polymer-like, low-frequency behavior. The mechanical signature of supramolecular structures is a low-frequency shoulder to the alpha relaxation as evidenced in many other monoalcohols<sup>10,10,23–28</sup> and some polyalcohols.<sup>47,48</sup> In the phenylpropanols, the feature is less pronounced than in the prototypical monoalcohol, 2-ethyl-1-hexanol. This is consistent with a smaller separation between Debye and alpha processes in the dielectric spectrum of the phenylpropanols. There is no obvious ordering between the propanols of the slow mechanical contribution: In 3P1P, the slow contribution at high temperatures is prominent and the crossover to purely viscous flow happens at even lower frequencies than for 1-propanol (see Figure 3(c, d) and Supporting Information).

On the high-frequency side of the mechanical alpha process, the spectra of all the phenylpropanols are very similar except for the secondary processes that are slightly different in intensity and temporal separation from the alpha relaxation. This supports the suggestions of an underlying generic alpha relaxation shape put forward by Gainaru and co-workers for rheological spectra<sup>49–51</sup> and Pabst et al. for light scattering spectra.<sup>33</sup> The general picture in both cases is that the spectral relaxation shape of the alpha process is generic and deviations from this generic shape come from the addition of separate processes on the low- and high-frequency side.

The dielectric Debye and alpha processes seem to be strongly coupled in the phenylpropanols as the separation of the two processes does not change with temperature. This is interesting because the general observation is that the two processes have a nonmonotonic time scale separation suggesting that they merge at high and low temperatures.<sup>52</sup> Our finding is based on the premise of additivity of Debye and alpha processes and a purely exponential Debye relaxation. Additivity is commonly assumed when modeling the full spectra and certainly works when the processes are well separated. In the case of the phenylpropanols, the two processes are completely merged and a different assumption might change the picture slightly. However, there is no sign of the two processes separating in the spectrum at any of the measured temperatures, thus indicating that the temperature dependence of the separation cannot be big in any of the phenylpropanols. We note that Böhmer et al.<sup>1</sup> reached the same conclusion for 1P1P, but not for 2P1P and 3P1P, when comparing lightscattering alpha peak frequency and dielectric (Debye) peak frequency. The discrepancy could stem from the uncertainty introduced when comparing two different methods measured under different experimental conditions.

Having established that the phenylpropanols indeed display the typical features of monoalcohols—in that the main peak in their dielectric spectra should be viewed as a merged Debye-like peak and alpha relaxation—we note that the dielectric spectra of the phenylpropanols are atypical for monoalcohols in two ways that are both related to intensity:





**Figure 4.** Time scales of dielectric and shear mechanical spectra. (a) Loss peak frequencies of dielectric Debye and  $\alpha$  as well as the shear mechanical  $\alpha$  loss peak. (b) Time-scale indices. For each temperature where both a shear and a dielectric spectrum were recorded, the frequency associated with the shear peak was divided by the frequency of the  $\alpha$  relaxation as found from the dielectric spectrum taken at the same temperature. DC704 data is taken from Jakobsen et al.<sup>44</sup> (c) Debye and  $\alpha$  peaks.

- Normally, when Debye and alpha are not well-separated, the intensity of the dielectric Debye peak is low, as seen in e.g. 4-methyl-3-heptanol, where the two processes have roughly the same intensity, or in 3-methyl-3-heptanol, where the Debye is almost absent.<sup>7,8,10</sup> For most neat systems, relative dielectric strengths are roughly proportional to relative time scales of Debye and alpha  $\epsilon_{D,\max}'' / \epsilon_{\alpha,\max}'' \propto f_{D,\max} / f_{\alpha,\max}$ <sup>25</sup> meaning that large separation in time scales usually correlates with a large Debye intensity and small separation in time scales with less intense Debye process. All the phenylpropanols have a fairly high overall intensity but a small separation in time scales. In this respect, the phenylpropanol spectra are more similar to the spectra from glycerol and other polyalcohols.
- Normally, the intensity of the dielectric alpha process in monoalcohols ( $\epsilon_{\max}'' \approx 10^{-1}$ ) is below the value expected from microscopic arguments.<sup>2</sup> In the phenylpropanols, it is clear in Figure 3(a) that the intensity of the alpha process (the high-frequency wing) is 10 times higher than that of 2E1H. Thus, the remaining alpha process has a loss peak maximum around 1, when a Debye is subtracted from the spectrum (more details in the Supporting Information). This pattern could be general for phenylpropanols as similar dielectric spectra were found for different phenylalcohols.<sup>53,54</sup> The second anomaly is also valid for 1-propanol, but not the first. This again seems to be general for other normal primary alcohols (at least up to 1-undecanol).<sup>55,56</sup>

It is not obvious what the cause for these anomalies is. The general interpretation of the low intensity of the alpha process in monoalcohols is that part of the dipole moment is locked in the supramolecular structure.<sup>2,15</sup> Using that logic, the relatively high intensity of the alpha process in the propanols could be due to less rigid/more transient structures formed in these alcohols

where individual molecules have more freedom to move independently. Another possibility is that on average fewer molecules are involved in chain structures thus giving the alpha peak more intensity. Both explanations align well with the fact that the low-frequency process sometimes observed in depolarized light scattering seems to be present only in branched monoalcohols,<sup>30,31</sup> and was speculated to be reminiscent of the chain relaxation, i.e., that the orientation of molecule is only allowed to decorrelate fully once the chain has relaxed. No low-frequency process is found in 1-propanol or phenylpropanols in the light scattering spectra.<sup>1</sup>

In conclusion, our mechanical measurements of the phenylpropanols display low-frequency (subalpha) behavior that suggests the existence of polymer-like aggregates of linear hydrogen-bonded structures. The shear spectra have nearly identical shapes if the secondary relaxations are neglected, thus supporting the notion of a generic alpha relaxation shape. We find that the shear alpha relaxation time is faster than the dielectric alpha relaxation, and that the dielectric Debye and alpha relaxation time scales have a temperature independent separation suggesting that the two time scales are strongly coupled in the phenylpropanols.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcb.2c07120>.

Multiple data sets for several of the propanols as well as a comparison to the previously published dielectric data; the procedure for isolating the dielectric alpha peak shown in more detail, for all compounds and all temperatures; and unscaled derivative plots for all compounds and all temperatures (PDF)

## AUTHOR INFORMATION

## Corresponding Author

Tina Hecksher – Glass and Time, IMFUFA, Department of Science and Environment, Roskilde University, Roskilde 4000, Denmark; [orcid.org/0000-0002-6048-6095](https://orcid.org/0000-0002-6048-6095);  
Email: [tihe@ruc.dk](mailto:tihe@ruc.dk)

## Authors

Mathias Mikkelsen – Glass and Time, IMFUFA, Department of Science and Environment, Roskilde University, Roskilde 4000, Denmark; [orcid.org/0000-0001-6494-2644](https://orcid.org/0000-0001-6494-2644)

Jan Philipp Gabriel – Glass and Time, IMFUFA, Department of Science and Environment, Roskilde University, Roskilde 4000, Denmark; [orcid.org/0000-0001-7478-6366](https://orcid.org/0000-0001-7478-6366)

Complete contact information is available at:

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## Notes

The authors declare no competing financial interest.

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