Hydrogen Bonding Exchange and Supramolecular Dynamics of Monohydroxy Alcohols

Shinian Cheng,[1,*] Shalin Patil,[2] and Shiwang Cheng[2,†]
[1]*Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA*
[2]*Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan 48824, USA*

(Received 28 August 2023; accepted 3 January 2024; published 29 January 2024)

We unravel hydrogen bonding dynamics and their relationship with supramolecular relaxations of monohydroxy alcohols (MAs) at intermediate times. The rheological modulus of MAs exhibits Rouse scaling relaxation of $G(t) \sim t^{-1/2}$ switching to $G(t) \sim t^{-1}$ at time τ_m before their terminal time. Meanwhile, dielectric spectroscopy reveals clear signatures of new supramolecular dynamics matching with τ_m from rheology. Interestingly, the characteristic time τ_m follows an Arrhenius-like temperature dependence over exceptionally wide temperatures and agrees well with the hydrogen bonding exchange time from nuclear magnetic resonance measurements. These observations demonstrate the presence of Rouse modes and active chain swapping of MAs at intermediate times. Moreover, detailed theoretical analyses point out explicitly that the hydrogen bonding exchange truncates the Rouse dynamics of the supramolecular chains and triggers the chain-swapping processes, supporting a recently proposed living polymer model.

DOI: 10.1103/PhysRevLett.132.058201

Hydrogen bonding (H-bonding) is one of nature's most fundamental interatomic interactions. It is present in alcohols, water, and many biomacromolecules like proteins, RNA, and DNA, and plays an important role in molecular recognition [1,2], sensing [3], and medication [4–6]. However, a fundamental understanding of the H-bonding interaction and dynamics is far from achieved, especially when H-bonding interaction induces supramolecular structures. For instance, monohydroxy alcohols (MAs), one of the simplest H-bonding liquids, exhibit Debye relaxation [7] from their supramolecular structures, whose origin remains a topic of active debate [8–19]. Recent studies correlate the Debye relaxation with the end-to-end reorientation of MAs with chain structures [11,17,19–21], which initiates speculations of dynamic modes in MAs in analogy to the normal modes of type-A polymers [22]. Although recent studies show signs of supramolecular dynamics at intermediate times in some MAs [21], it is not clear whether or how these dynamics correlate with the subchain motions. Even less is known about the bridging rules between the reversible H-bonding association or dissociation, i.e., the H-bonding dynamics, and the supramolecular dynamics. Since the H-bonding exchange is much faster than the terminal relaxation of MAs [10,18,21,23], the supramolecular dynamics at intermediate times should serve as a key to unraveling the relationship between H-bonding dynamics and supramolecular dynamics of MAs.

Recently, a *zero-free-parameter* living polymer model (LPM) has been proposed to connect the H-bonding dynamics with the supramolecular structure formation and dynamics of MAs [20]. Specifically, the LPM predicts the emergence of an intermediate time associated with the chain breakage τ_B that divides the supramolecular dynamics. For a given supramolecular chain, Rouse dynamics of the supramolecular chains prevail at time $t < \tau_B$. At $t > \tau_B$, chain swaps, which speeds up the end-to-end vector reorientation of the supramolecular chain leading to Debye relaxation at $\tau_D = (\tau_B \tau_\alpha \bar{N}^2)^{1/2}$, with τ_α being the structural relaxation and $\bar{N}$ the characteristic chain length. Although a scaling of $\tau_D \sim \tau_\alpha^{1/2}$ has been observed recently [20], *no* experiments have been performed to delineate the characteristics of τ_B and its relationship with τ_D and H-bonding dynamics, which represent the key differences of LPM from other models, including the transient chain model (TCM) [18], the chain-g_k fluctuation [11] with g_k being the Fröhlich-Kirkwood factor, and the dipole-dipole cross-correlation mechanism (DDCM) [24,25].

In this Letter, we delineate the supramolecular dynamics of MAs with chain structures at intermediate times and elucidate their relationship with the H-bonding dynamics. Different from previous efforts, we rely on new rheological measurements of stress relaxation and relaxation time distribution analyses for dielectric spectra to obtain a complete characterization of supramolecular relaxation without or with active dipolar changes. 2-ethyl-1-hexanol (2E1H), 5-methyl-2-heptanol (5M2H), 2-butyl-1-octanol (2B1O), and *n*-butanol (nBL) have been chosen as model systems due to their known supramolecular chain formation [8]. Poly(propylene glycol) with a number average molecular weight of 4 kg/mol (PPG4k) is included for comparison due to its similar separation between τ_α and τ_f with 2E1H (Fig. 1). Details of materials and methods are presented in Supplemental Material (SM) [26].

Figure 1 presents the relaxation modulus, $G(t) = \sigma(t)/\gamma_0$, of 2E1H after a step deformation of $\gamma_0 = 10\%$ at a shear rate

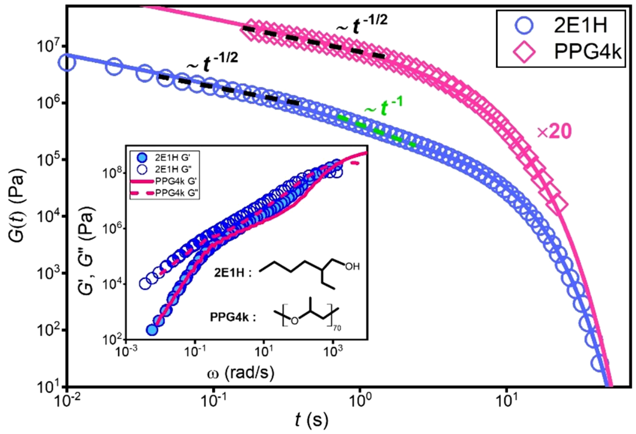

FIG. 1. The relaxation modulus $G(t)$ of 2E1H (blue) and PPG4k (pink, 20 times vertical shift) after a step deformation. The blue solid line shows the fit from Eq. (1), and the pink solid line represents $G(t) \sim (\tau_f/t)^{1/2} \exp(-t/\tau_f)$. The inset gives the storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ of 2E1H (blue symbols) and PPG4k (pink lines) as well as their molecular structures.

of $\dot{\gamma} = 0.5\ \mathrm{s}^{-1}$ and $T = 158$ K. The $G(t)$ of PPG4k at $T = 213$ K after $\gamma_0 = 10\%$ is presented for comparison. The time resolution of the stress relaxation experiments is ~0.01 s, which is much longer than $\tau_\alpha = 2.1 \times 10^{-3}$ s of 2E1H and $\tau_\alpha = 3.8 \times 10^{-4}$ s of PPG4k at the testing temperatures. Thus, the stress relaxation provides dynamics slower than τ_α, emphasizing the supramolecular nature. For PPG4k, a power law of $G(t) \sim t^{-1/2}$ is observed followed by an exponential decay with a terminal time τ_f. The relaxation function can be well described by $G(t) \sim (\tau_f/t)^{1/2} \exp(-t/\tau_f)$ (the solid pink line in Fig. 1), which is consistent with the Rouse model [28]. On the other hand, 2E1H exhibits dynamics slower than τ_α due to the supramolecular structures. A two-step relaxation can be resolved that divides the relaxation curve into three regions: region I, $G(t) \sim t^{-1/2}$ (Rouse scaling) before some intermediate time τ_m^R; region II, $G(t) \sim t^{-1}$ between τ_m^R and τ_f; and region III, $G(t) \sim \exp(-t/\tau_f)$ at $t > \tau_f$. Experimentally, the single mode terminal relaxation in region III of 2E1H echoes with the Debye relaxation of 2E1H and $\tau_f \approx \tau_D$ holds [20]. One can obtain an extrapolated relaxation function for the stress relaxation of 2E1H (see Sec. 9 in SM [26]):

$$G(t) = A * \left(\frac{\tau_m^R}{t}\right)^{1/2} \exp\left(-\frac{t}{\tau_m^R}\right) + B * \left(\frac{\tau_m^R}{t}\right) \exp\left(-\frac{t}{\tau_f}\right)\left[1 - \exp\left(-\frac{t}{\tau_m^R}\right)\right], \qquad (1)$$

with A and B being two fit parameters (the solid blue line in Fig. 1). The first term on the right-hand side of Eq. (1) describes the Rouse dynamics of region I, and the second term covers regions II and III. Different from PPG4k with the Rouse dynamics dominating the whole stress relaxation, Rouse modes of 2E1H end at τ_m^R before the terminal relaxation τ_f, highlighting the influence of the reversibility of H-bonding interaction. These observations indicate rich supramolecular dynamics of MAs at intermediate timescales.

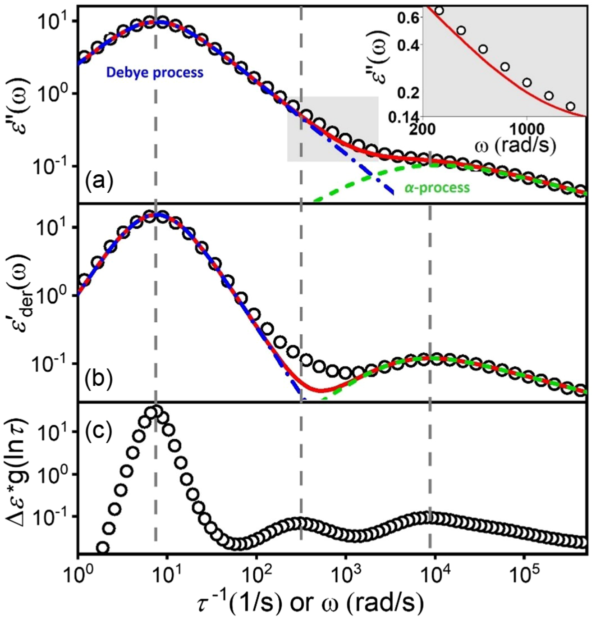

FIG. 2. (a) The dielectric loss permittivity $\varepsilon''(\omega)$ and (b) the derivative spectra $\varepsilon'_{\mathrm{der}}(\omega)$ of 2E1H. (c) The relaxation time distribution density function $\Delta\varepsilon * g(\ln\tau)$ of 2E1H. All spectra and analyses were at $T = 171$ K. The inset of (a) shows the amplification of the highlighted region of $\varepsilon''(\omega)$.

To confirm the revealed Rouse dynamics and to resolve the physical mechanism dictating the crossover between region I and region II, we turned to broadband dielectric spectroscopy (BDS). H-bonding-induced supramolecular chains are accompanied by an accumulation of dipoles along the chain backbone. If Rouse modes of the supramolecular chains exist, BDS should be able to resolve them [22]. Figure 2 presents the dielectric loss permittivity $\varepsilon''(\omega)$ [Fig. 2(a)] and derivative spectra of the storage permittivity [29], $\varepsilon'_{\mathrm{der}}(\omega) = -(\pi/2)[\partial\varepsilon'(\omega)/\partial\ln\omega]$ [Fig. 2(b)], at $T = 171$ K, where ω is the angular frequency. The corresponding storage permittivity $\varepsilon'(\omega)$ is presented in Fig. S1 of SM [26]. Two characteristic peaks can be resolved from $\varepsilon''(\omega)$ or $\varepsilon'_{\mathrm{der}}(\omega)$ with the peak at higher frequencies being the structural relaxation and the peak at the lower frequencies the Debye relaxation. We fit the storage and loss spectra with one Debye function (dash-dotted blue line) and one Havriliak-Negami (HN) function (dashed green line). The derivatives of them were employed to fit the derivative spectra [Fig. 2(b)]. The solid red lines are the sum of these two functions. A clear short in the dielectric amplitude has been observed at intermediate frequencies between the sum and the experiments in both $\varepsilon''(\omega)$ and $\varepsilon'_{\mathrm{der}}(\omega)$, especially in $\varepsilon'_{\mathrm{der}}(\omega)$. We note that a recent study [30] also commented on the challenge of fitting the spectra of other MAs at the intermediate frequencies, which is in agreement with our observations. These observations thus suggest the presence of new relaxation processes between τ_α and τ_D.

To better resolve the new relaxation processes, we have further performed relaxation time distribution analyses [31–33] that can resolve weak or overlapping processes (see Sec. 1.3 in SM [26]). This is especially effective for MAs with strong Debye relaxation. Figure 2(c) presents the relaxation time distribution, $\Delta\varepsilon * g(\ln\tau)$ with $\Delta\varepsilon$ being the dielectric amplitude and $g(\ln\tau)$ the density function, of 2E1H. An intermediate relaxation process is resolved between τ_α and τ_D, confirming the new supramolecular dynamics of 2E1H at intermediate times not anticipated by the prevailing TCM [18], chain-g_k fluctuation mechanism [11], and DDCM [24,25]. In the following, we focus on the supramolecular dynamics and their relationship with the H-bonding dynamics, which distinguishes the current contribution from previous works [11,12,15,17,20]. We rely primarily on the relaxation time distribution analyses to identify the intermediate processes to avoid large errors from the fit of introducing another HN function [30].

Figure 3 plots a comparison of characteristic relaxation times of 2E1H revealed by rheology and BDS: the structural relaxation, τ_α^R and τ_α^{BDS}, the intermediate relaxation, τ_m^R and τ_m^{BDS}, and the Debye and the terminal time, τ_D and τ_f. Here, the superscript R represents rheology and BDS denotes dielectric measurements. τ_α^{BDS} and τ_α^R, as well as τ_D and τ_f, follow identical temperature dependence although τ_α^R (or τ_f) is ~2.7 times faster than τ_α^{BDS} (or τ_D). The rheology relaxation time could be slightly different from the BDS measurements owing to the different techniques probing the same physical processes [34]. Interestingly, similar temperature dependence is observed between τ_m^{BDS} and τ_m^R at their overlapping temperatures and $\tau_m^{\text{BDS}} \approx \tau_m^R$. These results suggest a similar physical origin between τ_m^{BDS} and τ_m^R: the Rouse motions of supramolecular chains. In the following, we use τ_m to represent τ_m^{BDS} or τ_m^R. Interestingly, detailed analyses of τ_m show an Arrhenius-like temperature dependence over a wide temperature range and times (10^{-7} to 10^{-2} s), where both τ_α and τ_D (or τ_f) follow super-Arrhenius temperature dependence. A noticeable deviation from the Arrhenius temperature dependence is observed for τ_m at temperatures close to T_g, which will be discussed later.

To the best of our knowledge, the above experiments and analyses provide the *first* direct support for the presence of Rouse dynamics of MAs with supramolecular chain structures that do not exist in the TCM [18], the chain-g_K fluctuation [11], and the DDCM [24,25]. On the other hand, a recently proposed LPM [20] does predict the emergence of Rouse dynamics up to the chain breakage at τ_B. Specifically, the LPM predicts conventional polymer dynamics at $\tau_\alpha < t < \tau_B$ when chain breakage has not yet taken place [Figs. 4(a) and 4(b)]. For unentangled polymer melts, Rouse modes control dynamics slower than τ_α, and a relaxation modulus scaling $G(t) \sim t^{-1/2}$ is anticipated. If no chain breakage takes place before the longest Rouse time of the unentangled polymer, $\tau_B \gg \tau_c \approx \tau_\alpha \bar{N}^2$, the end-to-end reorientation of the supramolecular chains will be accomplished through Rouse dynamics. As long as $\tau_B < \tau_c$, the chain breakage takes place at τ_B, which truncates the Rouse dynamics and facilitates the end-to-end reorientation of MAs [Figs. 4(b) and 4(c)].

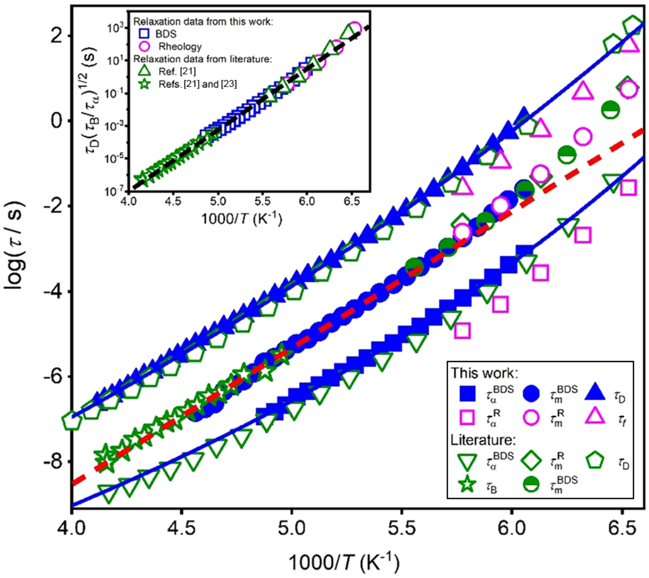

FIG. 3. Relaxation times of 2E1H from dielectric spectroscopy, rheology, and NMR. The blue filled and pink open symbols are dielectric and rheology results of the current study. The blue lines are fits to the Vogel-Fulcher-Tammann [35–37] equation: $\log_{10}\tau = \log_{10}\tau_0 + 0.434[DT_0/(T - T_0)]$, with fit parameters being presented in Table S1 of SM [26]. The green symbols are literature results of τ_α^{BDS} [21], τ_m^R [21], τ_m^{BDS} [21], τ_B (from NMR) [23], and τ_D [21]. The dashed red line shows the Arrhenius-like temperature dependence of τ_B and τ_m over wide temperatures. Inset: $\tau_D(\tau_B/\tau_\alpha)^{1/2}$ following Arrhenius temperature dependence.

Therefore, the LPM explains the $G(t) \sim t^{-1/2}$ at intermediate times. However, the LPM further predicts the Rouse scaling ends at τ_B. One has to compare τ_B with τ_m to enable a full examination of the LPM since both rheology and dielectric spectroscopy do *not* provide direct quantification of τ_B. Figure 3 compares τ_B of 2E1H from nuclear magnetic resonance (NMR) experiments (green stars) [23] with τ_m from rheology or dielectric spectroscopy. Remarkably, $\tau_B \approx \tau_m$ is observed at their common temperature region that covers ~1.5 decades in time. Furthermore, τ_B from NMR measurements follow identical Arrhenius temperature dependence as τ_m. These observations thus suggest the chain breakage through H-bonding exchange truncates the Rouse dynamics [Figs. 4(a) and 4(b)] before the terminal relaxation [Figs. 4(a)–4(c)], supporting the LPM.

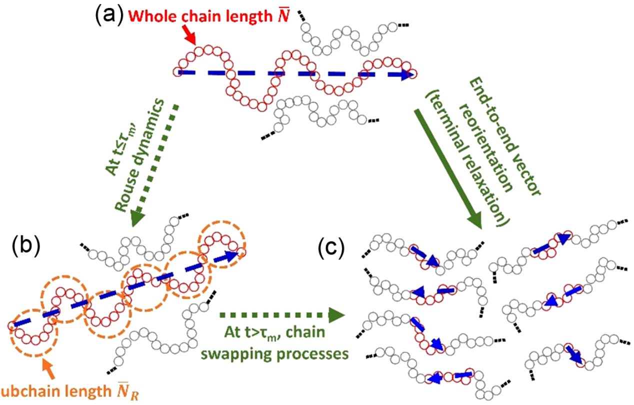

FIG. 4. Relaxation mechanism of MAs with chain structures, where the gray and red circles represent individual alcohol molecules. The chains with red and gray circles are the test and surrounding chains. The dashed blue arrows represent the end-to-end vector of the test chain or subchain. (a) A representative test chain with a length $\bar{N}$ and end-to-end vector at $t = 0$. (b) At $\tau_\alpha < t \leq \tau_m$, chain breakage has not yet taken place and Rouse dynamics dominate. A subchain with size $\sqrt{t/\tau_\alpha}$ accomplishes its relaxation at time t, and $\bar{N}_R \approx \sqrt{\tau_m/\tau_\alpha}$ is the characteristic subchain size that finishes the end-to-end reorientation at τ_m. (c) At $t > \tau_m$, chain breakage must happen. Chain swapping leads to the fragmentation of the original chain (the red circles), which facilitates the end-to-end vector reorientation.

Both the rheology and dielectric measurements point to (i) an Arrhenius temperature dependence of τ_m over wide temperatures and (ii) slight deviation of τ_m from the Arrhenius temperature dependence taking place at temperatures close T_g. In addition, the rheological measurements reveal stress relaxation switching from $G(t) \sim t^{-1/2}$ to $G(t) \sim t^{-1}$ at τ_m. Can the LPM explain these new observations that have not been anticipated by any other existing theories or models? According to LPM [20],

$$\tau_m \approx \tau_B \approx \frac{1}{k_2\bar{N}} \approx \sqrt{\frac{2}{c_0 k_1 k_2}}, \tag{2}$$

with k_1 and k_2 the reaction rate constants of H-bonding association and dissociation, c_0 is the molar concentration of MAs in the supramolecular chains, and $\bar{N} = \sqrt{c_0 k_1/(2k_2)}$ is the characteristic supramolecular chain size [20]. Since k_1 and k_2 follow Arrhenius temperature dependence, Eq. (2) gives an Arrhenius temperature dependence of τ_B when the temperature dependence of c_0 is small. At low temperatures, c_0 might change due to the polymerization with reversible bonds [38,39], leading to a deviation of τ_B from Arrhenius temperature dependence. Indeed, nice Arrhenius temperature dependence is obtained at the whole temperature range when one plots $\tau_B\bar{N} \equiv 1/k_2 = \tau_D(\tau_B/\tau_\alpha)^{1/2}$ bypassing the $\bar{N}$ (or c_0) in the analyses (Fig. 3 inset). We note that $1/k_2$ represents the lifetime of H bonding, which is challenging to obtain in the deep supercooled region [40–42]. Therefore, LPM explains well the Arrhenius temperature dependence of τ_m as well as its deviation from the Arrhenius temperature dependence close to T_g.

Regarding the switch in stress relaxation from $G(t) \sim t^{-1/2}$ to $G(t) \sim t^{-1}$ at τ_m, a first principle derivation is not available at this moment that requires a detailed description of the chain-swapping process. However, LPM predicts $\tau_B = \tau_m \approx \tau_\alpha \bar{N}_R^2$, with $\bar{N}_R$ being the characteristic sizes enjoying full relaxation at τ_B [Figs. 4(a) and 4(b)]. According to the Rouse model, the modulus at τ_m is $G_R \sim 1/\bar{N}_R$. On the other hand, the full end-to-end vector reorientation relaxation [Figs. 4(a)–4(c)] of the supramolecular chain with length $\bar{N}$ takes place at τ_f with a modulus $G_f \sim 1/\bar{N}$. Thus, $G_R/G_f \sim \bar{N}/\bar{N}_R \approx (\tau_m/\tau_f)^{-1}$. Thus, LPM anticipates the scaling of $G(t) \sim t^{-1}$ between τ_m and τ_f when active chain swapping takes place. The hold of $\bar{N}/\bar{N}_R \approx (\tau_m/\tau_f)^{-1}$ [or the observation of $G(t) \sim t^{-1}$] gives $\tau_f \approx \tau_m * \bar{N}/\bar{N}_R$, indicating a chain to go through $\bar{N}/\bar{N}_R$ times (on average) breakage to achieve a full end-to-end reorientation. Note that $\tau_f \approx \tau_m * \bar{N}/\bar{N}_R = 1/(k_2\bar{N}_R)$; the end-to-end reorientation of the supramolecular chain can be understood through the effective breakage of subchain of sizes $\bar{N}_R$ [Figs. 4(b) and 4(c)] as discussed previously [20]. These analyses thus provide a clear illustration of the relationship between the H-bonding lifetime and the supramolecular dynamics of MAs, including the Debye relaxation [Figs. 4(a)–4(c)].

To examine the robustness of the obtained understanding, we have further performed rheology and dielectric measurements for two other MAs, i.e., 5M2H and 2B1O, and reanalyzed the dielectric and NMR results of nBL [18,43]. The stress relaxation of 5M2H and 2B1O (Fig. S3 in SM [26]) shows a two-step stress decline beyond the structural relaxation with $G(t) \sim t^{-1/2}$ switching to $G(t) \sim t^{-1}$ before τ_f. Furthermore, the relaxation time distribution analyses (Fig. S4 [26]) offer clear signatures of the intermediate processes, whose characteristic times agree well with τ_m from rheological measurements and show Arrhenius-like temperature dependence over wide temperatures (Fig. S5 [26]). For nBL, τ_m agrees excellently with τ_B at their common temperatures (Fig. S6 [26]). Note that 2E1H and nBL are the only two MAs with systematic dielectric and NMR measurements in the existing literature, and $\tau_m \approx \tau_B$ is found in both MAs. Given the key element of τ_B of TCM [10,18], the observed $\tau_m \approx \tau_B$ might suggest a connection between LPM and TCM. Nevertheless, these observations support the *universality* of the revealed Rouse dynamics and the H-bonding exchange mediated chain-swapping dynamics before the end-to-end reorientation.

In conclusion, we have performed novel rheological measurements and new analyses for dielectric spectra to delineate supramolecular dynamics of MAs with chain structures. Rheological measurements of MAs exhibit Rouse scaling of $G(t) \sim t^{-1/2}$ that changes to $G(t) \sim t^{-1}$ at time τ_m before their terminal relaxation. At the same time, dielectric analyses reveal new relaxation processes between τ_α and τ_D with characteristic time comparable with τ_m from rheology. Detailed analyses show τ_m have near Arrhenius temperature dependence at high and intermediate temperatures, while slight deviations from the Arrhenius temperature dependence have been observed close to T_g. Moreover, τ_m from rheology and dielectric measurements agree remarkably well with the H-bonding exchange time from NMR measurements. The observations thus reveal rich supramolecular dynamics of MAs at intermediate times and two outstanding features of the relationship between the H-bonding dynamics and dynamics of MAs: (i) the H-bonding exchange truncates Rouse dynamics of MAs and (ii) the H-bonding exchange mediates chain-swapping processes at intermediate times. These results have not been anticipated by TCM [18], chain-g_k fluctuation [11], and DDCM [24,25], and provide the first direct experimental support to a recently proposed living polymer model. In addition, the developed quantitative description of the dynamics of MAs [Eq. (1)] also distinguishes the current study from these previous efforts including ours [11,18,20,24,25], enabling future fingerprinting dynamics of MAs at fine time and length scales. These results thus lay down a solid foundation for further elucidations of the relationship between H-bonding dynamics and supramolecular dynamics of H-bonding liquids, including the Debye relaxation—a puzzle in the field for more than 100 years [8]. We have noticed that recent studies observed a slow Arrhenius process (SAP) in polymers [44–46]. Although the connection is not clear at this moment between τ_m or τ_B of MAs and the SAP, further studies should provide insights on the relationship between them.

This work was supported by the Michigan State University Discretionary Funding Initiative (MSU-DFI). The authors thank Professor Böhmer Roland's group for their generosity in sharing their dielectric spectra of n-butanol at high temperatures involving frequencies of 1 MHz to 1 GHz.

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[*] Corresponding author: scheng235@wisc.edu

[†] Corresponding author: chengsh9@msu.edu

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