From Strong to Fragile Glass Formers: Secondary Relaxation in Polyalcohols

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(Received 10 August 2001; published 14 February 2002)

We have studied details of the molecular origin of slow secondary relaxation near T_g in a series of neat polyalcohols by means of dielectric spectroscopy and ^{2}H NMR. From glycerol to threitol, xylitol, and sorbitol the appearance of the secondary relaxation changes gradually from a wing-type scenario to a pronounced β peak. It is found that in sorbitol the dynamics of the whole molecule contributes equally to the β process, while in glycerol the hydrogen bond forming OH groups remain rather rigid compared to the hydrogens bonded to the carbon skeleton.

DOI: 10.1103/PhysRevLett.88.095701 PACS numbers: 64.70.Pf, 61.25.Em, 77.22.Gm

Dynamics in supercooled liquids and glasses faster than the structural relaxation are often summarized by secondary relaxation processes [1,2]. In dielectric spectroscopy secondary relaxation can be seen in the loss spectra by excess contributions to the primary process, either by a shoulder or by a second peak [1,3–9]. A systematic investigation of these processes which are not attributed to intrinsic degrees of freedom [10] was already performed by Johari and Goldstein more than three decades ago [1,11]. It seems that the high frequency excess contributions are common features of supercooled liquids. Up to now the molecular origin of the β relaxation is an open question [12–14]. Even the subdivision of glass formers into two classes which show either the excess shoulder or a well defined β peak in the dielectric loss was proposed [12]. However, recent investigations on glycerol have demonstrated impressively the close relationship between both [9].

We have investigated a series of the neat polyalcohols glycerol, threitol, xylitol, and sorbitol from temperatures far above the glass transition down to below T_g. Instead of investigating mixtures with different compositions [15,16] our homolog series allows for studying dynamics in pure systems. Glycerol, threitol, and sorbitol were purchased from Aldrich. Xylitol was obtained from Fluka. OD selectively deuterated compounds were prepared in our lab, while glycerol-D_5 and sorbitol-D_4, deuterated at the end groups, were purchased from Deutero. Glycerol [17–21] and sorbitol [6,13,14,22–24] are well known glass forming liquids, which differ significantly in the fragility, following the definition of Angell. In addition, while in sorbitol a pronounced β peak was found in the dielectric loss [13,14,23,24], in glycerol an excess contribution at the high frequency wing of the α process is observable [18].

For a first characterization of the four polyalcohols dielectric loss spectra were recorded using standard techniques. Dielectric permittivity was determined using the frequency response analyzer Alpha (Novocontrol). For a direct comparison in Fig. 1 the spectra $\epsilon''(\nu)$ are shown for similar reduced temperatures $T/T_g \sim 1.08$. The peaks of the structural relaxation show up in the spectra at similar positions $\nu \sim 0.1$–0.3 Hz while their height depends significantly on the substance. A systematic variation of the occurrence of the β process is found. While for xylitol the peak structure is still observable, in threitol rather the high frequency wing prevails. For glycerol solely the wing scenario is present. It has to be noted that by scaling of the temperature by T_g the comparison of the data is somewhat arbitrary regarding the β process. Scaling by the secondary relaxation seems to be more appropriate. However, this requires the knowledge of the time scale of the fast process which is accessible only once a peak is visible. The inset in Fig. 1 shows the dielectric loss $\epsilon''(\nu)$ for sorbitol, xylitol, and threitol for temperatures

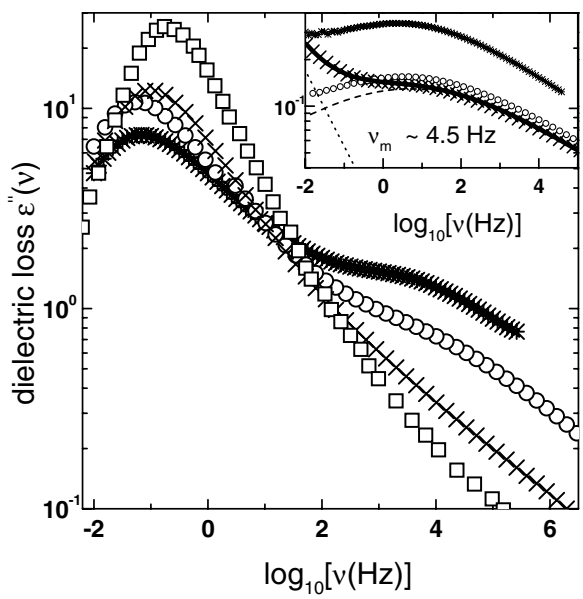

FIG. 1. The dielectric losses $\epsilon''(\nu)$ of glycerol (□), threitol (×), xylitol (∘), and sorbitol (∗) are plotted for temperatures 195, 230, 254, and 274 K, respectively. The inset shows data taken at 209 K (threitol), 198 K (xylitol), and 200 K (sorbitol) to adjust the time scales of the secondary relaxation. The lines are fitting curves as described in the text. The glycerol data were taken from [19].

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where the β-peak maximum occurs at $\nu_{\beta,\max} \sim 5$ Hz well separated from the α process. It is noted that even in threitol a pronounced β maximum is found although the data at higher temperatures shown in the main figure would direct to a wing-type behavior. Therefore, a classification of threitol into a wing-type or peak-type β-process glass former seems to be not meaningful.

The systematic trend found for the secondary relaxation goes along with the fragility of the polyalcohols quantified by the fragility index m (glycerol: $m = 57$, threitol: $m = 79$, xylitol: $m = 94$, and sorbitol: $m = 128$). From a comparison of glycerol and sorbitol, fundamental differences in the dynamics should be expected; however, the intermediate sized molecules threitol and xylitol demonstrate the gradual change in the fragility. In Fig. 2 the characteristic relaxation times are plotted for all substances as obtained by best fits of the $\epsilon''(\nu)$ data to a superposition of a Havriliak-Negami distribution [25] for the α process and a symmetric Cole-Cole distribution [26] for the β process. We want to stress that this evaluation method assumes statistical independence of both processes; however, significant errors should be relevant only when both time scales are on the same order. As an example for the quality, the fitting curves are shown for threitol at one temperature; see the inset in Fig. 1. Here the solid line represents the fitting curve while the dotted and dashed lines are the contributions of the Havriliak-Negami and the Cole-Cole distribution, respectively. At higher temperatures, the time scales of the primary and the secondary relaxation become too similar to allow for an unambiguous line-shape analysis. We have omitted these temperatures in our fitting procedure [27]. In sorbitol, xylitol, and threitol the β process shows an Arrhenius-like temperature dependence. Interestingly, by a crude extrapolation of the corresponding activation energies E_A and prefactors τ_0, see Fig. 2, in glycerol the resulting time scale of the β process at $T = 179$ K is in harmony with recent dielectric experiments in aged samples [9], $\tau_\beta \sim 5s$ [28]. The extrapolation for glycerol was performed by plotting E_A and $\log_{10}\tau_0$ versus the length N of the carbon skeleton and extrapolating in each case linearly to $N = 3$.

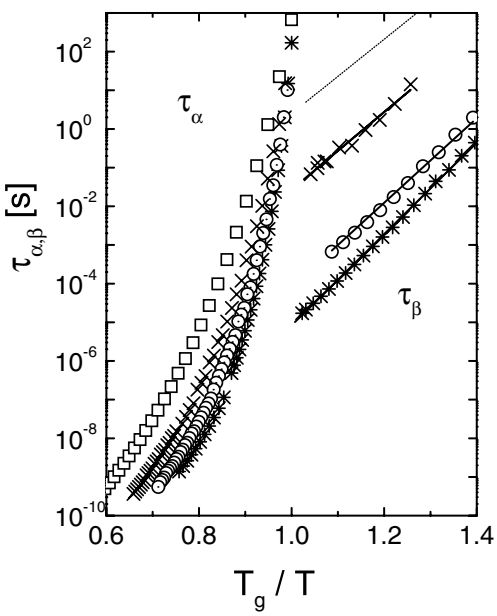

FIG. 2. Averaged relaxation times for glycerol (□), threitol (×), xylitol (∘), and sorbitol (∗). The straight lines through the τ_β data were fitted assuming thermally activated processes (threitol: $E_a = 43$ kJ/mol, $\tau_0 = 2.5 \times 10^{-12}$ s; xylitol: $E_a = 52$ kJ/mol, $\tau_0 = 1.0 \times 10^{-15}$ s; sorbitol: $E_a = 61$ kJ/mol, $\tau_0 = 1.3 \times 10^{-17}$ s. For glycerol the parameters were linearly extrapolated from the others, $E_a = 34$ kJ/mol, $\tau_0 = 6.3 \times 10^{-10}$ s (dotted line). The glycerol τ_α data were taken from [19].

The high values of the preexponential factor τ_0 (see caption of Fig. 2) can be understood by considering a temperature independent distribution of activation energies instead of a single value. The corresponding distribution of correlation times broadens with decreasing temperature [29]. Only the temperature dependence of the maximum value can be described with a preexponential factor comparable to the Debye time (10^{-14} s). The time averages $\langle\tau_\beta(T)\rangle$, however, reflect an apparent smaller preexponential factor $\tau_0 < 10^{-14}$ s, as found, e.g., in sorbitol. On the other hand, in threitol, and even more pronounced in glycerol, the time scale of the α process is much closer to the β process resulting in a partial preaveraging of the distribution of correlation times τ_β. This provides a rate averaged rather than a time averaged correlation time leading to an apparent preexponential factor $\tau_0 > 10^{-14}$ s.

In glycerol the temperature dependence of the α process shows relatively small curvature. This more Arrhenius-like behavior can be attributed to the network character due to hydrogen bonds. Sorbitol with a slightly larger ratio of hydroxyl groups to hydrogens at the carbon skeleton than glycerol, however, is as fragile as other molecular glass forming liquids without hydrogen bonds like toluene [12] or ortho-terphenyl [30]. It can be argued that with increasing molecular weight more hydroxyl groups are linked together intramolecularly through the carbon skeleton. These structural restrictions [31] counteract a homogeneous formation of hydrogen bonds, leading to a broader range of molecular interactions. Assuming that the distribution of interactions is somehow reflected by the nonexponentiality of the structural relaxation, the considerations made above are in harmony with the strong correlation between fragility and nonexponentiality observed in a large number of supercooled liquids [30].

Below T_g, the β peak can be determined from the dielectric susceptibility $\epsilon''(\nu)$ even for threitol; see the inset in Fig. 1. Assuming as a simple model of spatially restricted β dynamics a rotational random jump process on a fixed cone and neglecting any interactions between the molecular dipoles, the cone semiangles Θ can be extracted from the fitting results mentioned above. From analyzing random walk computer simulations [32] containing this

model the empirical relationship $\sin\Theta \approx (\Delta\epsilon_\beta/\Delta\epsilon_\alpha)^{1/2}$ was extracted, where $\Delta\epsilon_\beta$ and $\Delta\epsilon_\alpha$ are the areas of the β and the α peak, respectively [33]. In this analysis it was assumed that the α peak originates from an isotropic motion, determining the maximum possible $\Delta\epsilon$. The spatial restriction of the β process to a small angular region leads to $\Delta\epsilon_\beta < \Delta\epsilon_\alpha$. The smaller the amplitude of the fluctuations (Θ), the smaller $\Delta\epsilon_\beta$ is. Although this is a very rough approximation, the resulting angles plotted in Fig. 3 are in harmony with angles reported on other low weighted molecular glass formers [34,35].

To shed more light on the origin of the secondary relaxation, in the next step deuteron NMR is employed. By using compounds selectively deuterated at different molecular positions site specific dynamics can be probed [36]. Deuterons are ideal candidates to study molecular dynamics since the dominant quadrupolar interaction is a single particle interaction [36,37]. We have measured the spin-lattice relaxation times T_1 from the magnetization decays $\phi(t)$ of glycerol-D_5, -OD_3, sorbitol-D_4, and -OD_6 below T_g. By determining the rate average $\langle T_1^{-1}\rangle^{-1}$ from the initial slope of $\phi(t)$, contributions due to spin diffusion can be excluded [38,39]. This is especially important since spin diffusion significantly depends on the concentration of deuterons [40].

Both time scale and geometry of the rotational dynamics contribute to T_1 [34]. Assuming molecular dynamics slower than the inverse Larmor frequency, $\omega_L^{-1} \sim 4 \times 10^{-9}$ s, a rough connection between both contributions and T_1 can be considered as follows. The smaller the fluctuations are, the longer T_1. Assuming e.g., a two site rotational jump process, smaller angles between both positions would correspond to longer T_1 [34]. Slowing down of the dynamics also lead to an increase of T_1. By comparing the relaxation data of all four selectively deuterated compounds, interesting details of the dynamics can be extracted without further knowledge of molecular details. It has to be noted that the α process dominates T_1 only at higher temperatures $T > T_g$.

In Fig. 4, for $T < T_g$ the normalized spin-lattice relaxation times $T_1^{K_q} = K_q\langle T_1^{-1}\rangle^{-1}$ are plotted versus the reduced inverse temperature T_g/T. By multiplying with the quadrupolar coupling constant K_q, differences due to K_q are eliminated. The constants K_q were obtained by the standard technique analyzing the solid state powder spectra at 90 K for all substances. In sorbitol both compounds -D_4 and -OD_6 show the same spin-lattice relaxation, indicating that an overall molecular motion dominates the relevant relaxation process. $T_1^{K_q}$ of both glycerol-OD_3 and -D_5 are significantly longer than in sorbitol. This can be explained by assuming in glycerol slower dynamics and/or smaller amplitudes for the secondary relaxation than in sorbitol, which is in harmony with the observations from dielectric spectroscopy [9,41].

Interestingly, in glycerol the spin-lattice relaxation times of the deuterons at the hydroxyl groups are longer than at the carbon skeleton [42]. Assuming the time scale of the dynamics is the same at all positions, the differences in $T_1^{K_q}$ can be explained by smaller fluctuation amplitudes of the hydroxyl deuterons than the remaining deuterons. This interpretation supports the assumption of strong network character in glycerol due to hydrogen bonds. In sorbitol the network character is less marked; here all parts of the molecules contribute equally to the dynamics relevant for the secondary relaxation.

In conclusion, we have studied the dynamics of the homologous series of polyalcohols glycerol, threitol, xylitol,

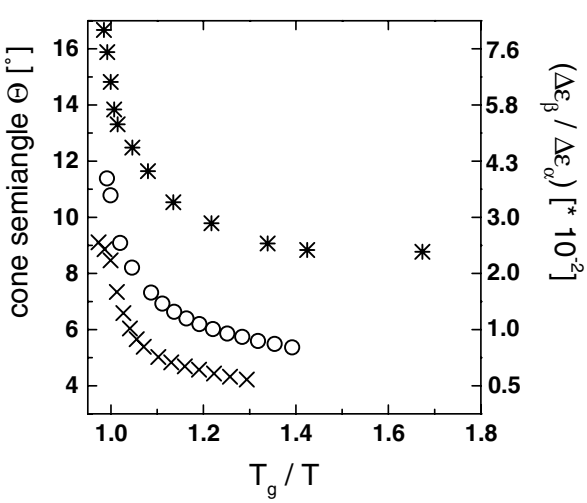

FIG. 3. Within a simple jump model for the β dynamics of spatially restricted motion a cone semiangle can be extracted; see text. On the right axis the corresponding fitting parameters are drawn. The symbols are ($\times$) threitol, ($\circ$) xylitol, and ($*$) sorbitol.

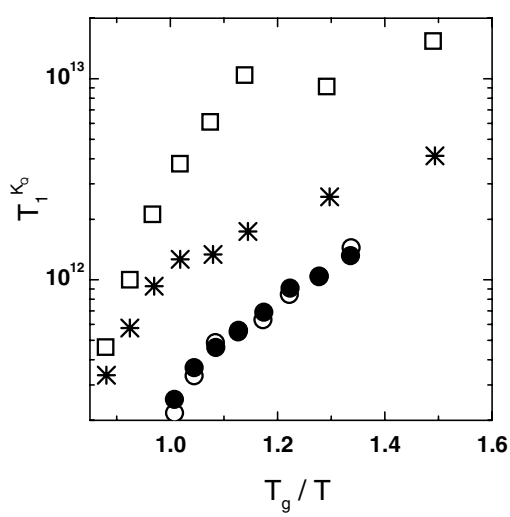

FIG. 4. Normalized spin-lattice relaxation times $T_1^{K_q}$; see text. While in glycerol OD ($\square$) and CD ($*$) bonds show significantly different dynamics; in sorbitol both OD ($\circ$) and CD ($\bullet$) deuterons have the same relaxation times $T_1^{K_q}$, indicating similar dynamics at all sites of the molecules.

and sorbitol. By means of dielelectric spectroscopy and ^{2}H-NMR systematic trends in the dynamic properties are found. With increasing molecular weight a gradual increase in the fragility is observed. From glycerol to sorbitol the appearance of the Johari-Goldstein β process changes from a wing-type behavior to a marked β-peak scenario. Even in threitol at low enough temperatures a β peak can be observed. Our findings strongly support the assumption that the excess wing is the high-frequency flank of a β relaxation.

Details of the origin of the β relaxation were studied by comparing selectively deuterated compounds. While in sorbitol deuterons at all positions probe a similar dynamics; in glycerol the OD bonds which are part of the hydrogen bond network are rather rigid compared to the hydrogens bonded to the carbon skeleton.

We thank R. Böhmer for helpful discussions and R. Richert for providing the sorbitol-D_4 sample. We thank H. Wagner for providing the dielectric relaxation data of sorbitol. We are indebted to A. Dörk for preparing several samples of partially deutered compounds. This project was supported by the Deutsche Forschungsgemeinschaft (SFB 262/Grant No. D9).

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