Thermal Glass Transition Beyond the Vogel-Fulcher-Tammann Behavior for Glass Forming Diglycidylether of Bisphenol A

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For the low molecular weight fragile liquid diglycidyl ether of bisphenol A we report, based on Brillouin and dielectric spectroscopy, on a thermal glass transition where the relaxation time of the α process does not go to infinity. Instead, the structural α relaxation disappears spontaneously at the transition point. That discontinuity in relaxation time coincides with a kink in the longitudinal hypersonic velocity and determines unambiguously the transition from the liquid to the glassy state.

In the past 20 years of theoretical and experimental work on glasses, a tremendous amount of details has been elucidated (e.g., [1–8]), but there was no breakthrough concerning the understanding of the thermal glass transition (TGT). The key question is still open: Does a phase transition from the liquid to the glassy state exist? The reason for little progress in the understanding of the TGT is probably due to contradictory experimental findings: The TGT shows kinetic (e.g., [2,9,10]) as well as phase transition features (e.g., [11–14]), which strongly interfere in the vicinity of the glass transition point T_g. Because of the significant increase of the structural α-relaxation time τ_α and the related kinetic features of the TGT, the majority of publications in the field supports the idea, that τ_α diverges below T_g according to a Vogel-Fulcher-Tammann (VFT) law and that every observable TGT is necessarily a crossover of τ_α with the involved experimental time scales. Hence, an eventually existing intrinsic glass transition point $T_{gs} < T_g$ is principally masked by this crossover phenomenon at T_g. Although widely accepted as a fact, the divergence of τ_α below T_g remains an extrapolation. Deviations from the VFT behavior [15,16] are observed and even a cutoff of τ_α has been reported for some glass formers [12–14]. In order to prove that an intrinsic glass transition can be a phase transition, one has (i) to find a glass forming material, where τ_α does not diverge and (ii) to choose the experimental conditions in such a way that crossovers between the α-relaxation process and experimental time scales involved are strictly excluded in the temperature interval around the TGT.

With respect to condition (i), we present diglycidyl ether of bisphenol A (DGEBA) as a low molecular weight ($M_w = 340\,\text{g/mole}$) glass forming model system with an α-relaxation time that unambiguously does not diverge. Based on time domain Brillouin spectroscopy (TDBS) [12,17,14] and dielectric spectroscopy (DES), we will show that DGEBA possesses an intrinsic glass transition at a well-defined transition temperature T_{gs}. Additionally,

it is determined by the discontinuous disappearance of $\tau_\alpha(T)$. That discontinuity is accompanied by a kink in the hypersonic velocity $v(T)$ at T_{gs}. We will show that $\tau_\alpha(T)$ follows a VFT law at temperatures above T_{gs}. Close to T_{gs}, however, $\tau_\alpha(T)$ starts to level and shows a cutoff at T_{gs}.

With respect to condition (ii), we have to take into account that usually two or more different time constants τ_i^{exp} are involved in any investigation of dynamic and static properties around the TGT: (a) the probe frequency $f = 1/(2\pi\tau_1^{\text{exp}})$, (b) the time scale τ_2^{exp} defined by the time constants involved in the cooling/heating regime for approaching the TGT. Using TDBS, the probe frequencies are in the gigahertz regime. Just above the TGT, τ_α is already in the range of minutes or hours, however. Therefore, the obtained hypersonic data represent so-called "frequency-clamped" properties measured in the "slow motion regime" with $\tau_\alpha/\tau_1^{\text{exp}} \gg 1$. However, with respect to other material-influencing effects such as temperature changes, the hypersonic moduli can relax (from $\tau_\alpha/\tau_2^{\text{exp}} \ll 1$ to $\tau_\alpha/\tau_2^{\text{exp}} \approx 1$). Hence, investigating the TGT of DGEBA with a high frequency probe at a "sufficiently slow" cooling rate should result either in a lower limit for the α relaxation and the intrinsic TGT or it should demonstrate that the TGT would shift according to the VFT law, $\tau_\alpha = \tau_{\alpha 0} e^{\Delta G/[R(T-T_0)]}$ ($\tau_{\alpha 0}$: attempt time; ΔG: free activation energy; R: universal gas constant; T_0: "freezing temperature") continuously towards T_0.

DES was performed in the plate condenser geometry at different temperatures in the range of 173–393 K. The dielectric spectra are obtained for the frequency range between $f = 10^{-2}$ and 10^5 Hz and were fitted using $\hat{\epsilon}(\omega) = \epsilon' - i\epsilon'' = -i(\sigma_{\text{dc}}/\omega\epsilon_0) + \sum_{k=\alpha}^{\gamma}\{\Delta\epsilon_k/[1 + (i\omega\tau_k)^{\nu_k}]^{\mu_k} + \epsilon_{\infty k}\}$ as a model function which contains the usual dipole relaxation processes (α, β, γ) of glass forming materials and a dc conductivity term. The quantities $\Delta\epsilon_k$ designate the relaxation strength, and the τ_k represent the related relaxation times. The $\epsilon_{\infty k}$
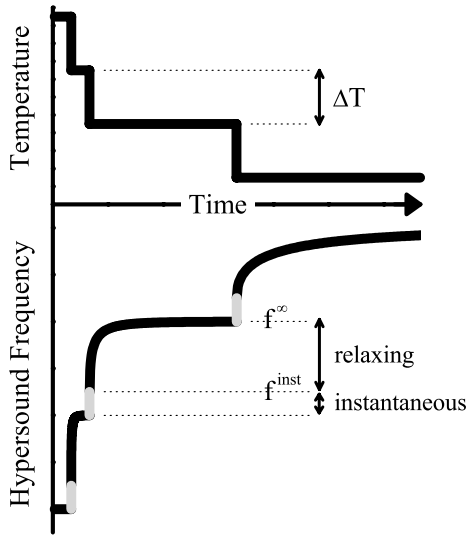
FIG. 1. Schematic description of TDBS measurements. Shown are three different temperature jumps and the resulting response of the hypersound frequency.

are the frequency-clamped dielectric constants related to the relaxation process k.

A detailed description of Brillouin spectroscopy has been given elsewhere (e.g., [17,18]). We use a modified tandem Brillouin spectrometer of the Sandercock type [17] with a solid state laser at $\lambda = 532$ nm. The backscattering technique is used to minimize temperature influence on the scattering angle and on the measured sound frequency data. The backscattering geometry provides the hypersonic wavelength $\Lambda = \lambda/(2n)$, where $n = n(T)$ is the temperature-dependent refractive index. Since usually the temperature coefficient of the sound velocity exceeds that of the refractive index by a factor of 10, we approximate $n(T)$ by its room temperature value. A typical TDBS experiment is shown in Fig. 1: Starting at higher temperatures ($T > T_{gs}$), temperature is lowered stepwise. With an accumulation time of 30 or 60 s, subsequent phonon spectra are recorded to get the temporal response of the hypersound frequency to the temperature perturbation. For the second temperature jump in Fig. 1, the response of the hypersound frequency f is explained in detail: There is an instantaneous increase in f to the value f^{inst}. After that, f relaxes towards the final value f^{∞}. Hypersound frequency data has to be collected for a sufficiently long time to be sure that f has reached its equilibrium value f^{∞} of the liquid state at given temperature (i.e., that f is either representative for f^{∞} or is sufficiently close to f^{∞} in order to give a reliable extrapolation). Evidently, a fast and precise temperature control of the sample is very important for the detection of sound frequency relaxations in the time domain. After a temperature step, temperature is stabilized within less than 2 min with a stability better than ± 0.025 K (Figs. 2 and 3) and without any measurable drift during the whole
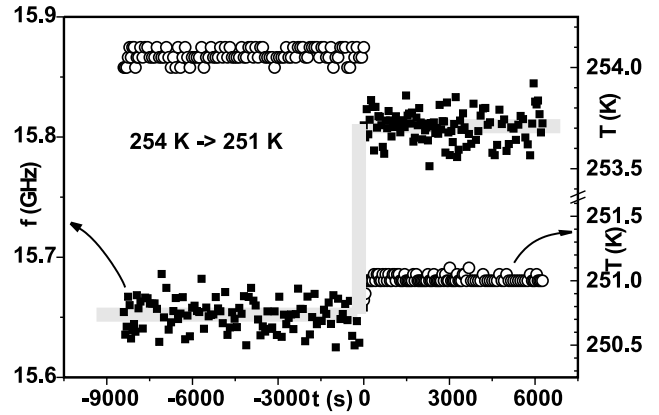

FIG. 2. Temperature step from 254 to 251 K (circles, right ordinate) at the reference time for the new temperature $t = 0$ and the related response of sound frequency (squares, left scale). The horizontal grey lines are least squares fits.

measurement. The sample itself is prepared as a film of about 100 μm thickness and is deposited directly on the heat exchanger. Thus, all relaxation times above some minutes can be resolved.

We used temperature steps of $\Delta T = -3(-2, -1)$ K depending on the distance from the TGT and measured simultaneously the evolution of the hypersonic frequency (Figs. 2–4). The relaxing part of the hypersound frequency f can be described by an adapted Kohlrausch-Williams-Watts (KWW) law $f(t) = f^{\infty} - (f^{\infty} - f^{\text{inst}}) \times e^{[-(t/\tau_\alpha)^\beta]}$ where f^{∞} is the relaxed value and β measures the distribution of the τ_α. The grey line for $t > 0$ in Fig. 3 is a nonlinear least squares fit according to the KWW equation. The average relaxation time is given as $\langle \tau_\alpha \rangle = \tau_\alpha/\beta \cdot \Gamma(\frac{1}{\beta})$, where the Gamma function yields the time average [19]. In a previous publication [12], we have shown for a polymer that the instantaneous frequency response per Kelvin of the liquid phase $f^{\text{inst}}/\Delta T$ corresponds to the frequency response per Kelvin of the glassy
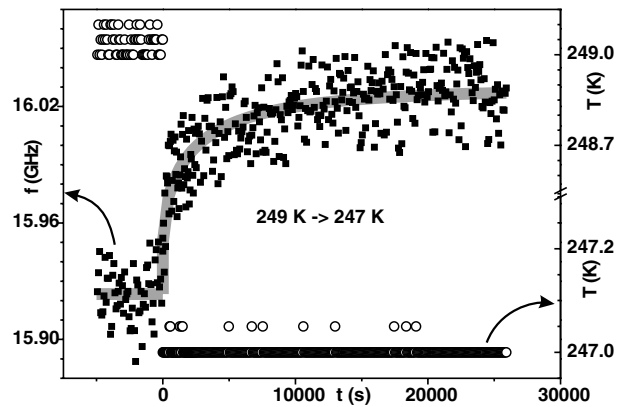

FIG. 3. Temperature step from 249 to 247 K (circles, right scale) and related sound frequency response (squares, left scale) (for further explanation, see text).
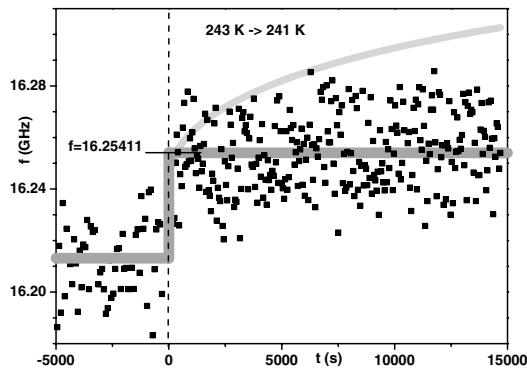
FIG. 4. Sound frequency response after a temperature step from 243 to 241 K. Dark grey lines: Linear least squares fits. Light grey curve: Extrapolation to fluid conditions (for further explanation, see text).

FIG. 5. Activation plot of the inverse averaged α-relaxation time of DGEBA as measured by DES and TDBS.

state. From this result, we conclude that $f^{\text{inst}}/\Delta T$ reflects predominantly the acoustic anharmonicity of the glassy state. TDBS is sensitive for relaxation processes larger than some minutes. Faster processes such as the secondary β-relaxation process are hidden in the instantaneous frequency response.

The values calculated for $\langle \tau_\alpha \rangle$ are presented in Fig. 5 for all measured temperature steps and the corresponding $f^\infty(T)$ are shown in Fig. 6. The step from 245 to 243 K was the lowest temperature-step still showing a relaxing sound frequency response as a consequence of the thermal excitation. The subsequent temperature step from 243 to 241 K gave only the instantaneous sound frequency response of the glassy state (Fig. 4). It is therefore obvious to determine $T_{gs} = 243$ K as the intrinsic TGT.

The linear fit to the data in Fig. 4 for $t \geq 0$ gives $f(t) = a - bt$ with $a = (16.2541 \pm 2 \times 10^{-4})$ GHz and $b = (2.3 \times 10^{-14} \pm 3 \times 10^{-13})$ GHz s^{-1}. Consequently, there is little space left for a hidden relaxation process below T_{gs}. In order to test further whether we could have missed experimentally the relaxing part, we have calculated the expected relaxation response on extrapolating the relaxation time $\tau_\alpha(243 \text{ K} \rightarrow 241 \text{ K})$ and the relaxed frequency $f^\infty(243 \text{ K} \rightarrow 241 \text{ K})$ of the hypothetical liquid state from relaxation time data of the previous temperature jumps. The measured results and the extrapolation are shown in Fig. 4. For the temperature step from 243 K $\rightarrow$ 241 K, it is obvious that either no relaxation processes exist any more or their relaxation times had jumped upwards by orders of magnitude.

It is not straightforward that relaxation times derived from different dynamic susceptibilities and different measurement techniques (e.g., dynamic and relaxation measurements) can be displayed in a single activation plot. Nevertheless, the sets of relaxation times derived from DES and TDBS fit very well which suggests that both experimental methods reflect the same relaxation process. Moreover, in an earlier publication [14] it was
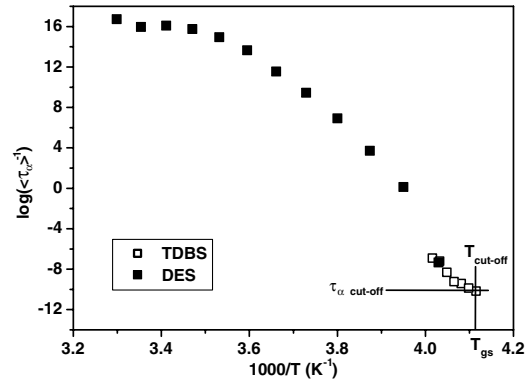
shown for a polymer that relaxation times derived from Brillouin measurement at higher temperatures (dynamic glass transition at Brillouin frequencies in the GHz regime) fit well to TDBS and DES relaxation data. Because of the relatively large scattering of the relaxing hypersound velocity, fitting of the experimental data to the KWW equation delivers relatively large errors in the distribution parameter β ($0 < \beta < 1$) of about ± 0.3. This makes any comparison of the distribution parameter between TDBS and DES measurements difficult. At $1000/T < 3.5$, the α relaxation (Fig. 5) shows the usual Arrhenius-like behavior, but at $3.5 < 1000/T < 4.1$ it meets the expected VFT law and even flattens out close to T_{gs} (Fig. 5). From pure DES data, we have calculated the reasonable values: $\tau_{\alpha,0} = 1.25 \times 10^{-13}$ s, $\Delta G = 8.3$ kJ mole^{-1}, and $T_0 = 220$ K.

The frequency response for the temperature step from 243 K $\rightarrow$ 241 K shows no relaxation at all (Fig. 4), and it does not reach the extrapolated sound frequency curve of the liquid state any more. As the result, DGEBA has a cutoff for τ_α within the immediate vicinity of $T_{gs} = 243$ K indicating a sudden disappearance of the α process.
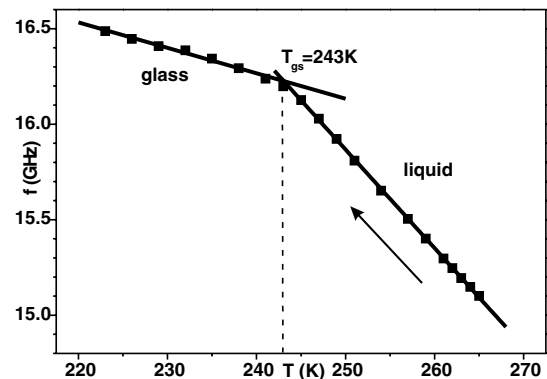

FIG. 6. Relaxed sound frequency as a function of temperature. The straight lines are fit curves. Arrow indicates cooling regime.

At the same temperature, the $f(T)$ curve shows a kink which, according to the genesis of the sound frequency data, is neither due to the crossover of the experimental time scale with the α process nor obscured by it. Therefore the kink indicates a spontaneous change of the acoustic properties at the TGT and, as a consequence, a steplike change of the longitudinal mode Grüneisen parameter at T_{gs} [17,20]. The underlying discontinuous change of the anharmonicity of the elastic potential gives a strong hint on the existence of an "isostructural" phase transition at T_{gs} but it cannot elucidate the transition mechanism. Another key role for the transition has the cutoff of the relaxation time at T_{gs}. Such a cutoff of relaxation times has been reported by Lüthy *et al.* [21] for the ferroelastic transitions of pure and mixed alkali cyanides and even for the transition into the orientational glassy state in between the critical concentrations. However, in contrast to the cyanide systems, our canonical glass shows no soft-mode behavior at all. On the other hand, using the phenomenological approach to structural phase transitions given by Müser *et al.* [22] (based on irreversible thermodynamics) and taking the elastic deformation and the temperature changes as external variables, we are able to describe qualitatively the temperature behavior of the frequency-clamped longitudinal sound velocity around T_{gs}. But again, the predicted softening of the static sound velocity is not observed [23]. Thus, we can speculate that the ideal glassy state is a randomly packed solid state with a minimum of free volume. Further investigations may show that the transition at T_{gs} could be explained by an extended mode coupling theory. A further inspection of our relaxation times shows a pronounced slope change of $1/\sqrt{-d\log(\tau_\alpha)/dT}$ as a function of T/T_{gs} at $T/T_{gs} = 1.15$. This slope change is even more pronounced than the one reported for salol [24]. This result is preliminary since our temperature range ends just above $T/T_{gs} = 1.2$.

In conclusion, an intrinsic glass transition exists for DGEBA approximately 20 K above the VFT-temperature T_0. A discontinuity in τ_α is shown for the first time at T_{gs} and is interpreted as a discontinuous change of the acoustic anharmonicity at the TGT. The spontaneous changes of both properties at T_{gs} have been confirmed recently for dibutyl phtalate and poly(vinyl acetate) [23] and thus corroborate the interpretation of the thermal glass transition as a phase transition.

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