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SHORT COMMUNICATION

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On the existence of an intrinsic glass transition in a fragile liquid: polyvinylacetate

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Abstract Time domain Brillouin spectroscopy has been used as a definitive experimental approach to demonstrate the intrinsic nature of the thermal glass transition in Polyvinylacetate. The transition from the equilibrium liquid to the ideal glassy state appears at the ultimate temperature T_{gs}.

Key words Glass transition – time dependent properties – high performance Brillouin scattering – Polyvinylacetate

The current discussion of freezing processes in liquids concerns the thermal glass transition (TGT) as well as the dynamic glass transition (DGT) characterized by their transition temperatures T_g and T^* well above T_g [cf. 1–3]. The DGT has been satisfactorily explained in the frame of mode coupling theory (MCT) [2]. Unfortunately, the MCT does not extend to the TGT, and until now there exists no other generally accepted model for the TGT. The difficulties in understanding the TGT are caused to a large extent by the appearance of extremely slow kinetic and relaxation processes in the vicinity of T_g which are difficult to handle in usual experiments. In the present experimental and theoretical situation the main question in the understanding of the TGT is whether i) there exists in the limit of sufficiently slow cooling an underlying phase transition [cf. 4] from the liquid to the ideal glassy state, or ii) the TGT simply reflects the cross-over of intrinsic relaxation times with typical time constraints of the experimental technique and the scientist's patience [cf. 2, 5].

The Polyvinylacetate (PVAC) under study is an atactic polymer with a molecular weight of $M_W = 91$ kg/mole showing a thermal glass transition temperature T_g at about 303 K. PVAC belongs to the class of ideal glass formers as it does not crystallize on any time scale although it undergoes a glass transition. As a consequence, PVAC can be held above its thermal glass transition in thermal equilibrium and only at excessive cooling rates does the material become supercooled. Hence, the aim of this paper is to show experimentally that at sufficiently slow cooling, the TGT in PVAC (as probably in other amorphous polymers) separates the quasi-ergodic liquid from the non-ergodic glassy state at the ultimate transition temperature T_{gs}. In addition, we will demonstrate the influence of the TGT on the ultra slow glass relaxation (α-relaxation) spectrum and prove the existence of a low frequency cut-off of the α-process.

In order to discriminate experimentally between the above-mentioned hypotheses, we applied the unconventional method of "time domain" Brillouin [6] spectroscopy (TDBS) to the PVAC. TDBS is understood as a spectroscopic method to investigate elastic properties in the Gigahertz regime. After a step-like temperature

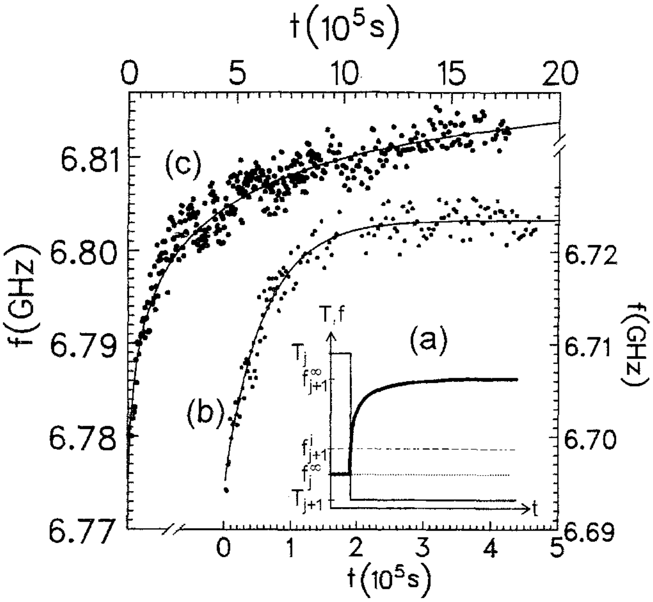

Fig. 1A Schematic representation of the temperature jump procedure: $T_{\mathrm{j}}, T_{\mathrm{j}+1}$: start and end temperature of the temperature step, respectively; $f_{\mathrm{j}}^{\infty}, f_{\mathrm{j}+1}^{\infty}$: fully relaxed sound frequency at T_{j} and $T_{\mathrm{j}+1}$, respectively; $f_{\mathrm{j}+1}^{\mathrm{i}}$: instantaneous frequency response after a temperature step $T_{\mathrm{j}} \rightarrow T_{\mathrm{j}+1}$; **B, C** Relaxing part of the sound velocity after temperature jumps from T_2 to T_3 and T_4 to T_5 as a function of time; –: fit curve

perturbance of the sample it is usually anticipated that far above T_{g} the elastic properties of the material equilibrate themselves as fast as its temperature does. Close, but still above T_{g}, where the structural glass relaxation times τ_{s} become extremely large, BS yields two kinds of information: a) with regard to the perturbance "strain", BS measures in the frequency domain the instantaneous elastic response in the slow motion regime ($\tau_{\mathrm{s}} v/\Lambda \gg 1$, where Λ is the hypersonic wavelength and v is the related sound velocity), b) with regard to the temperature jump, TDBS measures in the time domain extremely slow changes of the hypersonic frequencies f. Hence, close to the glass transition TDBS is able to measure extremely slow acoustic relaxation processes, which enables us to verify the existence of an intrinsic glass transition temperature in PVAC.

When all Brillouin experiments were performed using the 90A-scattering geometry [6] yielding $\Lambda^{90\mathrm{A}} = 363.8$ nm (vacuum laser wavelength $\lambda = 514.5$ nm), the sound velocity v was strictly proportional to the sound frequency and the influence of the optical refractive index on Λ definitely disappeared. Figure 1a schematically shows the "temperature jump" procedure we have used in order to study structural relaxations around the TGT of PVAC with BS. A temperature perturbation $\Delta T_{\mathrm{j}} = T_{\mathrm{j}} - T_{\mathrm{j}-1}$ causes an overall sound frequency response

$$\Delta f_{\mathrm{j}}(t) = \left[f_{\mathrm{j}}(t) - \lim_{t \to \infty} f_{\mathrm{j}-1}(t) \right]$$

$$= [f_{\mathrm{j}}(t) - f_{\mathrm{j}-1}^{\infty}] \quad (j = 1,2,3,\ldots)\,,$$

which generally evolves to the limiting value of the thermodynamic equilibrium $\Delta f_{\mathrm{j}}^{\infty} = (f_{\mathrm{j}}^{\infty} - f_{\mathrm{j}-1}^{\infty})$. The sound frequency relaxation due to a temperature perturbation can be measured in the time domain if its relaxation time τ_{s} is much larger than the recovery time of our thermostat τ_{th} (≈ 15 min). In the vicinity of T_{g} we have performed temperature steps of -3 K and -10 K and we have measured the frequency responses during time intervals ranging between 24 h and 5 weeks. A shorter recovery time τ_{th} would be helpful to extend the TDBS measurements to higher temperatures i.e., to faster relaxation frequencies. Because of the finite recovery time, one has to take care to suppress from the data analysis all data measured during this time and to verify the stability of the fit. If the frequency response is clearly dominated by the asymptotic behavior ($\tau_{\alpha} \rightarrow \tau_{\mathrm{th}}$), then the fitting procedure becomes arbitrary. In order to avoid the influene of nonlinear responses on the thermal glass transition we have based our analysis exclusively on the -3 K steps. The initial temperatures of the -3 K jumps are as follows: $T_0 = 312.2$ K, $T_1 = 309$ K, $T_2 = 306.2$ K, $T_3 = 303.1$ K, $T_4 = 300.4$ K, $T_5 = 297.5$ K, $T_6 = 294.6$ K. In Fig. 1b, c we show two representative sound frequency responses for temperature steps from T_2 to T_3 and from T_4 to T_5. The sound frequency response $\Delta f_{\mathrm{j}}(t)$ is composed of two parts: an instantaneous part $f_{\mathrm{j}}^{\mathrm{i}} - f_{\mathrm{j}-1}^{\infty}$ which responds as fast as the temperature recovery, and a slowly relaxing contribution $f_{\mathrm{j}}(t) - f_{\mathrm{j}}^{\mathrm{i}}$. Neglecting all data accumulated during the temperature recovery of the thermostat, each relaxing part could be fitted using a Kohlrausch–Williams–Watts (KWW) function [7] $[f_{\mathrm{j}}(t) - f_{\mathrm{j}}^{\infty}]/[f_{\mathrm{j}}^{\mathrm{i}} - f_{\mathrm{j}}^{\infty}] = \exp[-(t/\tau_{\mathrm{sj}})^{\beta_{\mathrm{j}}}]$ yielding the limiting sound frequency f_{j}^{∞}, the instantaneous frequency response $f_{\mathrm{j}}^{\mathrm{i}}$, the relaxation time τ_{sj} and the exponent β_{j}. From the time averaging of the KWW function an average relaxation time $\bar{\tau}_{\mathrm{s}} = (\tau_{\mathrm{s}}/\beta)\Gamma(\beta^{-1}) = \bar{f}_{\mathrm{s}}^{-1}$ can be calculated [cf. 2], where Γ is the gamma function. The choice of the KWW function as a model function for the fit of our hypersonic frequency responses was induced by the obvious stretched exponential behavior of the relaxing part.

The $f(T)$-curve shown in Fig. 2a contains the relaxed data determined for temperature jumps at $T_0, \ldots, T_7$(●), with several data resulting from -10 K jumps (□) , and -1 K jumps (·) within the glassy state. It is important to note that in contrast to hypothesis (ii) even the relaxed $f(T)$ curve consists of a linear high and a linear low temperature branch with a rather sharp kink which yields

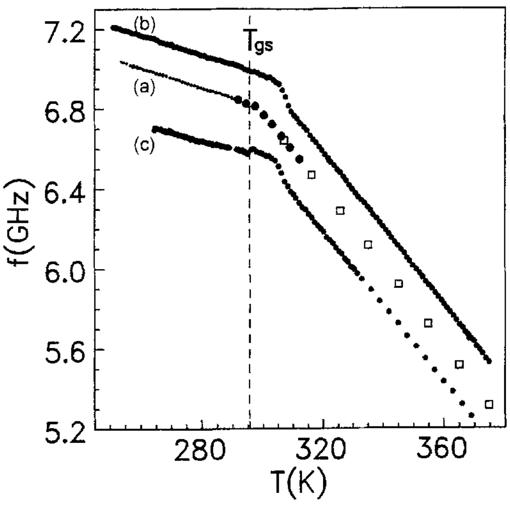

Fig. 2A Hypersonic frequency responses to temperature steps of -3 K (●), -1 K (·) and -10 K (□). **B** Hypersonic frequency response to temperature steps of $+1$ K, frequency shifted by $+0.2$ GHz. **C** Hypersonic frequency response to temperature steps of $+1$ K of a quenched sample, frequency shifted by -0.2 GHz

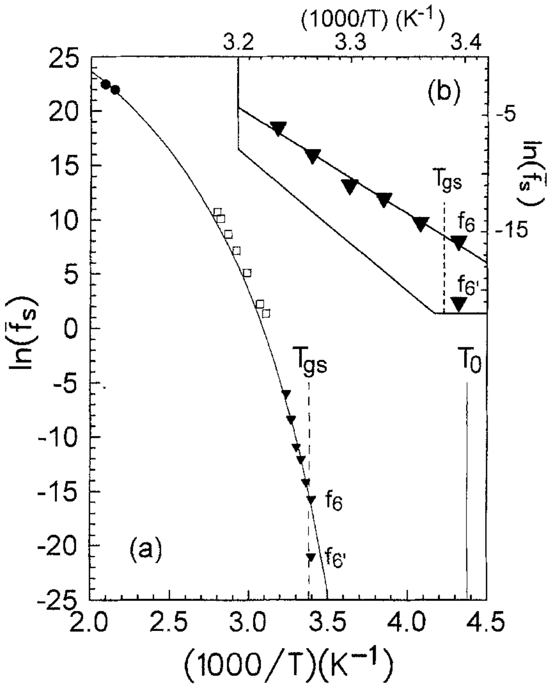

Fig. 3A Vogel–Fulcher plot of the relaxation frequencies $\bar{f}_s$ (▼) of the hypersonic frequency; ●: are the relaxation frequencies related to the wave vectors q^{90R} and q^{90A} ($q^{90R} > q^{90A}$) [6] ; □: dielectric relaxation data [9]. **B** Arrhenius behavior of the relaxation frequencies $\bar{f}_s$ (▼) of the hypersonic frequency; points at f_6 and $f_{6'}$: $\bar{f}_s$ of the KWW-fit with $\bar{f}^{\infty}(=f_6^{\infty})$ free and fixed $f^{\infty}(=f_{6L}^{\infty})$, respectively; T_{gs}: ideal glass transition temperature (further explanation see text)

an operative glass transition temperature $T_g = 297.3$ K. Figure 3b shows the relaxation frequencies $\bar{f}_s$ as a function of T^{-1}. It turns out that within the margin of error, $\bar{f}_s$ behaves Arrhenius-like over four orders of magnitude. Unfortunately, the apparent attempt frequency and the apparent activation enthalpy are unphysically high. Similar unphysically high parameters were recently found from dielectric time domain measurements for the α-process of amorphous Phenoxy (poly(bispenol-A, 2-hydroxypropylether)) [8]. According to ref. [1b] the unreasonably large magnitude of both values indicates the cooperativity of the related structural relaxation process. In this context it is of great interest to compare our relaxation frequencies measured in the time domain with own Brillouin data obtained in the frequency domain and with relaxation frequencies obtained from dielectric measurements [9]. Tentatively, we have fitted (Fig. 3a) all Brillouin data to a Vogel–Fulcher–Tamman (VFT) ansatz:

$$f_s = f_0 e^{\frac{-\Delta G}{R(T-T_0)}} .$$

In this case we obtain a rather reasonable activation enthalpy of $\Delta G = 29$ kJ/mole, a rather high attempt frequency $f_0^{\mathrm{VFT}} = 7 \cdot 10^{15}$ Hz, and an ultimative glass transition temperature $T_0 = 229$ K. T_0 is about 70 K below the T_g found by Brillouin spectroscopy. As a result, the VFT fit is compatible with data, but in order to respect the Arrhenius behavior of our low frequency data a very low T_0 is needed. The dielectric data from Ishida [9] are also in a rough agreement with the VFT curve although there is a systematic shift of the data with respect to our fit curve. It should be mentioned that usually (α)-relaxation times measured by classical Brillouin spectroscopy are shorter than related dielectric data. Of course, Brillouin spectroscopy measures with wave vectors close to zero and therefore probes the structural rearrangement. It should be stressed that **ab initio** there is no reason why dielectric and acoustic measurements probe the same relaxation processes, but as a matter of fact, the α-process usually seems to couple to the hydrodynamic modes probed by Brillouin spectroscopy [cf. 10]. This might be a consequence of the increasing cooperativity of the structural rearrangement on approaching the thermal glass transition.

The low frequency Brillouin data as well as the dielectric data deviate apparently from the curvature of the VFT fit. In order to evaluate the reliability of the VFT ansatz for the whole frequency range it should be stressed, that the curvature of the VFT curve is taken as a hint for the cooperativity of the freezing process. As a matter of fact, the actual VFT curve has its strongest curvature within the lower hypersonic frequency regime and becomes increasingly linear on approaching the thermal glass transition.

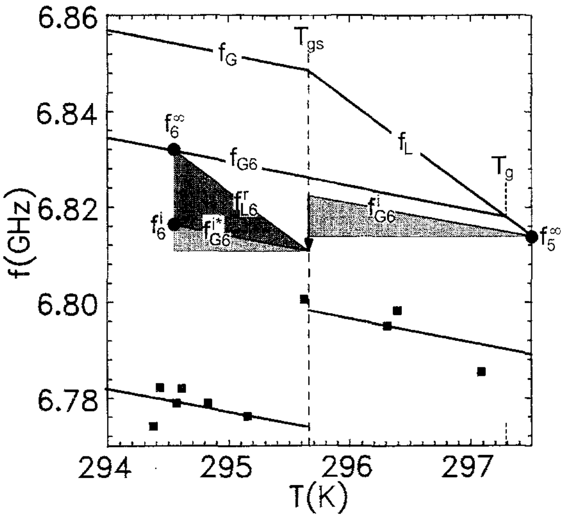

Fig. 4 Frequency response $f_5^\infty \rightarrow (f_6^i, f_6^\infty)$ at the temperature step from $T_5 \rightarrow T_6$;T_{gs}: ideal glass transition temperature, defined by the intersection of the straight lines f_{L6}^r and f_{L6}^{i*}; T_g: operative glass transition temperature, defined by the intersection of f_{G6} and a straight line through (T_5, f_5^∞) describing the frequency behavior of the liquid state; f_{G6}: straight line describing the linear frequency behavior of the glass; ■: hypersonic frequency of a quenched PVAC sample on stepwise heating towards liquid state (for further explanation see text)

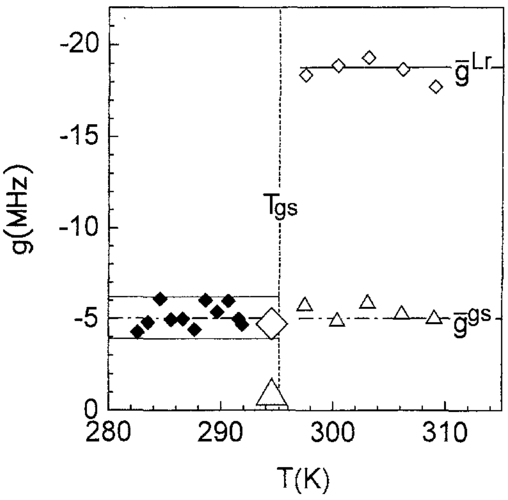

Fig. 5. Local temperature gradients g^{Lr} (◇), g^i (△), and g^{gs} (◆) of the sound frequency data in Fig. 2a; $\bar{g}^{Lr}, \bar{g}^{gs} = \bar{g}^i$: mean values of the respectively g_j^{Lr} and g_j^{gs}, g_j^i; T_{gs}: ideal glass transition temperature (further explanation see Fig. 3 and text)

It therefore seems to us that the VFT law is not able to describe the acoustic data in the whole temperature range until T_g and, of course, not very much below.

The sound frequency measured after the temperature jump from T_5 to $T_6 \leq T_g$ clearly still relaxes (Fig. 3b) but does not reach the related value of the liquid state (Fig. 2a). We have tried to force the least squares fit to this hypothetical limiting value, fixing it during the fit procedure. As a fit result, we obtained the average relaxation time $\bar{\tau}'_6 = 1.4 \cdot 10^9$ s whereas the free running fit yielded $\bar{\tau}_6 = 7 \cdot 10^6$ s. It is important to note that $\bar{\tau}_6$ corresponds perfectly with the Arrhenius plot through the data points $T_1, \ldots, T_5$ (Fig. 3b), but the large value of $\bar{\tau}'_6$ implies an abrupt increase of the average relaxation time of about two orders of magnitude. It is worth noting that the strong decrease of $\bar{\tau}'_6$ compared with $\{\bar{\tau}_1, \ldots, \bar{\tau}_5\}$ is completely incompatible with the Vogel–Fulcher plot for PVAC evaluated from dielectric data [9] and Brillouin data measured at high temperatures [11]. As shown in Fig. 3b and Fig. 4, all observations about relaxations in the time domain do end definitely at $T_6 < T_g$, the first data point in the glassy state. Summing up our observations, the hypersound data suggest: 1) a significant kink in the $f(T)$ curve at $T_g = 297.3$ K, corresponding to a discontinuity in the temperature derivative of the sound frequency and 2) an Arrhenius-like α-relaxation behavior which stops definitely at $T_6 = 294.6$ K with a minimal value of the relaxation frequency of about 0.1 μHz. In contrast to results obtained by dielectric time domain investigations on Phenoxy [8], there is no evidence for an Arrhenius-like continuation of the α-relaxation process well below T_g. The hypothesis that the relaxation process has a discontinuity between T_5 and T_6 seems to be unlikely. In order to support this view we have investigated the local temperature derivatives g_j^{Lr}, g_j^i and g_j^{gs} of the sound frequency data (Figs. 4 and 5) measured at $T_j (j = 0, \ldots, 7)$ defined by $g_j^{Lr} = (f_j^\infty - f_{j-1}^\infty)/(T_j - T_{j-1})$, $g_j^i = (f_j^i - f_{j-1}^\infty)/(T_j - T_{j-1})$ and $g_j^{gs} = (f_j^{gs} - f_{j-1}^{gs})/(T_j - T_{j-1})$. These temperature derivatives yield the hypersonic frequency response per Kelvin df/dT of the equilibrium liquid, of the instantaneous frequency response obtained immediately after temperature recovery of the sample, and of the glassy state respectively. The agreement between $\bar{g}^i$ and $\bar{g}^{gs}$ (Fig. 5) is a surprising result. It reflects the already frozen nature of PVAC with respect to a step-like temperature perturbation close to the TGT. g_6^i (△) plays an exceptional but decisive role, reflecting the passage from the liquid to the glassy state. Its value is significantly too low compared to $\bar{g}^i = \bar{g}^{gs}$, which is hard to understand if one believes in the instantaneous nature of this response.

Before discussing the quasi-static transition at T_{gs} it seems to be useful to discriminate between the different dynamic freezing processes observed at hypersonic frequencies: It is well known that the slope of the temperature dependence of the hypersonic frequency decreases at the transition from the fast motion ($\omega\tau \ll 1$) to the slow motion

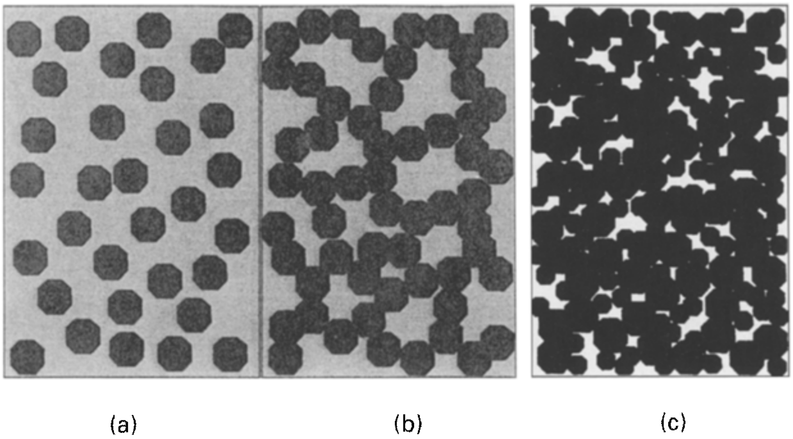

Fig. 6 Schematic representation of the cluster model (further explanation see text)

regime ($\omega\tau \gg 1$). However, the sound frequency temperature derivative differs appreciably from that of the glassy state [6]. In our case the hypersonic response investigated between 298 K and 360 K was measured in the slow motion regime with respect to the strain excitations yielding the temperature derivative of the liquid, frozen with respect to the strain fluctuations at hypersonic frequencies, i.e., $\bar{g}^{\mathrm{Lr}} \neq \bar{g}^{\mathrm{gs}}$. Only clamping the acoustic relaxations with respect to the temperature disturbance yields $\bar{g}^{\mathrm{i}} = \bar{g}^{\mathrm{gs}}$. In this sense there exist two dynamic freezing processes: i) the cross-over of the α-relaxation time with the rate of hypersonic deformation, ii) the cross-over of the α-relaxation time with cooling rate.

The TDBS results obtained in the vicinity of T_{gs} might be understood using the following hypotheses: i) PVAC exhibits an intrinsic glass transition temperature T_{gs}. ii) already well above T_{gs}, clusters of minimal free volume are formed within the liquid state (Fig. 6a). The amount of these clusters and probably their size increase on approaching the thermal glass transition, iii) at T_{gs} these clusters, being free of α-relaxations, coagulate and form a network of glassy cluster chains (Fig. 6b). The density of this network depends on the starting temperature (history) for the ultimate jump into the glassy state. Depending on the mass density of the network and the interconnection of the clusters, the coagulated structure exhibits a decreased absolute sound frequency compared to that of the ideal glassy state (Fig. 6c and Fig. 4). This renormalization of the sound frequency causes a jump of the instantaneous sound frequency response at T_{gs}. This jump compensates exactly for the missing part of the instantaneous frequency response at T_6. iv) Due to the quick temperature passage across T_{gs} some liquid phase still exists in the voids built by the cluster chains (Fig. 6b). This liquid can relax further towards the density of the ideal glassy state. This relaxation process depends on the instantaneously coagulated state at T_{gs}. The relaxation amplitude is determined by the temperature derivative $g_{\mathrm{j}}^{\mathrm{Lr}}$ and the ideal (intrinsic) glass transition temperature T_{gs}. v) After the temperature of the sample has crossed T_{gs} and the sample has completely relaxed, the sample finally reaches a certain glassy state which might be characterized by T_{g} (Fig. 4). Further relaxations due to the thermal glass transition do not appear. In turn, the experimental results together with the hypotheses (i.–v.) allow the construction of T_{gs}. As shown in Fig. 4 the data point (T_6, f_6^{i}) together with $\bar{g}^{\mathrm{gs}}$ define the straight line $f_{\mathrm{G6}}^{\mathrm{i*}}$ and (T_6, f_6^{∞}) together with the temperature derivative $\bar{g}^{\mathrm{Lr}}$ define the line $f_{\mathrm{L6}}^{\mathrm{r}}$, which both intersect at $T_{\mathrm{gs}} =$ 295.7 K.

The above findings have been verified (Figs. 2c, 4 ■) by inspecting the attack of acoustic relaxations towards thermal equilibrium in the time domain within a quenched PVAC sample of the same parent material. In order to display the onset of "melting", we applied small temperature steps of $+1$ K to the sample but recorded the Brillouin spectra only after an adapted temperature delay time. At $T = 294.8$ K this delay time was 4 h, but no onset of relaxations of the sound frequency towards equilibrium was observed. The first indications of such relaxations were only found at $T = 295.6$ K. In order to approach the thermal equilibrium we annealed the sample at this temperature over a period of 70 h and then continued our BS measurements, again performing $+1$ K steps. As a matter of fact, the hypersonic frequency curve shows a discontinuity close to the proposed T_{gs} of 295.7 K, supporting the idea of a thermoreversible transition at T_{gs}. At temperatures above T_{gs} a remarkable overheating effect was observed. A similar overheating effect was observed before (Fig. 2b) on the well annealed sample which was cooled down by the temperature-jump technique (Fig. 2a).

The overheating features shown in Fig. 2b, c demonstrate that even if the glassy state becomes unstable at T_{gs}, the melting of the cluster chains requires more time than was spent in this particular experiment.

We summarize our main results as follows: i) using "time domain" Brillouin spectroscopy, we found a phase transition-like phenomenon at a well defined transition temperature T_{gs} in the freezing regime of atactic PVAC. The fully relaxed sound frequency shows in the limit of infinite small temperature jumps a thermoreversible kink at T_{gs}, which characterizes the ideal glassy state, ii) at T_{gs} the instantaneous frequency response per Kelvin shows under usual experimental conditions a discontinuity which disappears if T_{gs} accidentally becomes the target of a temperature jump from above, iii) close to T_{gs} the average relaxation times of the α-process behaves Arrhenius-like, becoming as large as $7 \cdot 10^6$ s and displaying a cut-off.

A final comment should be added to the usually observed kinetic character of the thermal glass transition: it should be stressed that in the vicinity of the thermal glass transition the structural relaxation due to the involved temperature changes are so slow (Fig. 3) that most of the experiments done in the field suffer from the cross-over between internal relaxation times and the experimental time scale. As a consequence, even above T_{gs}, the glass forming liquid usually falls out of thermal equilibrium and shows the non-equilibrium behavior which has been reported and discussed in numerous publications. Nevertheless, at least in Polyvinylacetate the underlying "phase transition" exists which stops every relaxation towards the equilibrium state of the liquid. In order to further explain the nature of this transition it would be of great interest to generalize our results to other canonical glasses on the one hand and to find out the related order parameter on the other. In relation to findings in spin glasses [cf. 12], the investigation of non-linear response functions seems promising.

References

1. a) Ngai KL (1994) "Universal Patterns of Relaxations in Complex Correlated Systems", in "Disorder Effects on Relaxation Processes", Richert/Blumen, Springer-Verlag, Berlin, Heidelberg
   b) Donth E (1992) "Relaxation and Thermodynamics in Polymers", Glass transition, Akademie-Verlag, Berlin
2. Götze W, Sjögren L (1992) Rep Prog Phys 55:241
3. Matsui J, Odagaki T, Hiwatari Y (1994) Phys Rev Lett 73:2452
4. a) Gibbs JH, DiMarzio EA (1958) J Chem Phys 28:373
   b) Gee G (1970) Contemp Phys 11: 313
5. Kovacs AJ, Aklonis JJ, Hutchinson JM, Ramos AR (1979) J Polym Sci: Polym Phys Ed 17:1097
6. Krüger JK (1989) in 'Optical Techniques to Characterize Polymer Systems', Ed. by Bässler H, Elsevier, Amsterdam, Oxford, New York
7. Williams W, Watts DC (1970) Trans Faraday Soc 66:80
8. Alegría A, Guerrica-Echevarría E, Telería I Colmenero J, (1993) Phys Rev B 47:14857
9. Ishida Y, Matsuo M, Yamafuji K, Koll ZuZ Polymere (1962) 180:108
10. a) Patterson GD (1977) Journal of Polymer Science 45:455
    b) Patterson GD (1980) Methods of Experimental Physics 16A:170
11. Krüger JK, Bohn K-P, to be published
12. Fischer KH, Hertz JA (1991) "Spin Glasses", Cambridge