

## Beta Relaxation versus High Frequency Wing in the Dielectric Spectra of a Binary Molecular Glass Former

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The binary molecular glass former 2-picoline in tri-styrene is investigated by means of broadband dielectric spectroscopy with the aim of understanding the role of secondary relaxation processes that emerge during the glass transition. It is shown that the “high frequency wing,” which is seen in neat picoline, becomes a separate process in the mixture and exhibits all the features of a Johari-Goldstein relaxation. In particular, the previously found relation between activation energy and  $T_g$  is recovered. In addition, below  $T_g$  the width parameter of this secondary relaxation is shown to be governed by a common temperature dependence, and the time scale is characterized by an isokinetic point. Above  $T_g$  pronounced deviations from an Arrhenius behavior are observed.

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The evolution of the dynamic susceptibility in super-cooled liquids covers a broad dynamic range, in which a variety of relaxational features appear as the glass transition temperature  $T_g$  is approached. These properties are readily accessible by dielectric spectroscopy, and, in particular, the line shape of the main relaxation ( $\alpha$  process), and the properties of various secondary relaxations that appear at frequencies above the structural  $\alpha$  peak are topics of current research [1–3]. One type of process commonly referred to as Johari-Goldstein (JG)  $\beta$  relaxation was given particular attention, as it was clearly shown to occur in simple rigid molecules [4,5]. NMR studies have supported the notion that a small angle restricted reorientation of basically all molecules underlies the JG  $\beta$  relaxation [6]. On the other hand, many substances show only a simple power law [high frequency (HF) wing] at frequencies above the main relaxation peak. It was suggested to classify glass formers with respect to their secondary processes [7]: Those substances in which a pronounced and well separated JG secondary relaxation peak is detected were called “type B” glass formers, whereas systems that exhibit a simple power law at high frequencies were called “type A.” It has been a matter of controversial discussion whether this classification is justified and several authors have challenged this view by stating that the HF wing might just be some kind of JG  $\beta$  process [1,8–10]. Further insight into this problem may be gained by systematic investigation of binary mixtures, as we demonstrate in the following.

As compared to neat systems, binary glass formers so far have been studied to a lesser extent. As far as dielectric studies of low-molecular-weight binary systems are concerned often nonpolar glass formers were investigated by dissolving polar molecules to probe the dynamics of the nonpolar solvent, e.g., [11]. Recently dielectric and

NMR spectroscopy were used to systematically compare the dynamics in neat and binary low-molecular-weight glass formers [12,13].

In this Letter we investigate the dynamics of the respectively smaller component of binary mixtures of large and small molecules, namely, 2-picoline in various oligostyrenes (tri-styrene:  $M_n = 370$  g/mol; OS-1000:  $M_n = 1020$  g/mol; OS-2000:  $M_n = 2140$  g/mol) and 2-picoline in *o*-terphenyl. Because of the difference in the dipole moments of both substances in a mixture, the dynamics of the picoline molecules is selectively monitored by the dielectric experiment. As a neat glass former 2-picoline is known to be a type A system; i.e., only a HF wing is seen at frequencies above the  $\alpha$  peak. In the mixture, however, it turns out that the spectral shape strongly depends on the concentration  $c$  of 2-picoline, ranging from a pronounced secondary relaxation peak at low and intermediate concentrations to a simple power law (HF wing) for  $c \approx 1$  cf. Figs. 1 and 2.

In the following we particularly focus on mixtures of 2-picoline and tri-styrene, which we have investigated by differential scanning calorimetry and by dielectric spectroscopy (DS). In order to access secondary relaxations in a broad frequency window we have combined frequency and time-domain techniques so that a dynamic range from  $10^{-6}$  up to  $10^7$  Hz was covered. The picoline content of the mixtures was varied from 5% to 100% (by weight). The 2-picoline ( $M = 93$  g/mol,  $T_g = 133$  K) was purchased from Sigma-Aldrich and tri-styrene ( $T_g = 233$  K) from Polymer Standards Service. Tri-styrene was obtained as a distilled sample in order to have a monodisperse substance and to minimize the contribution of ionic conductivity.

The dielectric spectra were recorded with an impedance analyzer Schlumberger SI 1260 combined with a

broad band dielectric converter by Novocontrol in the frequency range of  $10^{-2}$  up to  $10^7$  Hz. In addition, time-domain measurements were carried out using a modified Sawyer-Tower setup similar to the one described in [15]. After Fourier transforming the time-domain data, both data sets were combined yielding spectra as shown in Figs. 1 and 2.

In a previous study it was shown that a secondary relaxation peak emerges out of a HF-wing scenario in the spectra of (neat) polyalcohols [8]. The spectra shown in Fig. 2 suggest a similar behavior in the present class of binary systems, and, indeed, one may speculate that both HF wing and  $\beta$  peak represent the same relaxation process. In order to verify this statement in the framework of a quantitative analysis, a phenomenological approach was chosen that is able to represent a HF wing in terms of a secondary relaxation peak that shows a power law on the HF side of the loss maximum. We used a set of empirical distributions of correlation times already introduced in [2,14]. The function used for the main relaxation is based on a generalized  $\Gamma$  distribution, whereas the  $\beta$  process is described by a distribution function that is compatible with a temperature independent distribution of activation energies and, at the same time, yields power laws at both sides of the relaxation maximum. In cases where both processes are seen within the experimental frequency window, the Williams-Watts (WW) approach [16] is applied to combine the two distribution functions. Thus, depending on the time constants for each process,  $\tau_\alpha$  and  $\tau_\beta$ , either a HF-wing scenario or a separate  $\beta$  peak is reproduced. An exponent  $\gamma$  characterizes a power law  $\omega^{-\gamma}$  that represents either the HF slope of the  $\beta$  relaxation peak or the high frequency wing, respectively.

In order to obtain the time constants of the  $\beta$  process also in cases where only a power law instead of a full secondary relaxation peak is seen within the experimental frequency window (i.e., at high picoline concentrations and at low temperatures), the relaxation strength of

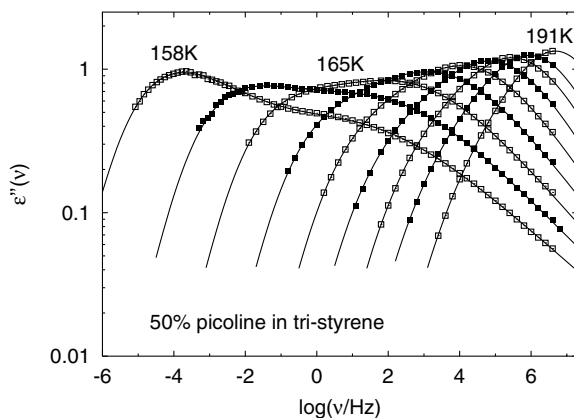


FIG. 1. The dielectric loss of 50% 2-picoline in tri-styrene. Solid lines are interpolations using appropriate model functions together with the Williams-Watts approach [2,14].

the  $\beta$  process  $\Delta\varepsilon_\beta(T)$  was extrapolated in a straightforward manner from the values found at higher temperatures and concentrations, respectively.

As can be inferred from Figs. 1 and 2, although neither 2-picoline nor tri-styrene (not shown) as neat substances exhibit a discernible  $\beta$  peak, a strong JG type relaxation process is seen in the mixture. For the main relaxation time  $\tau_\alpha$  (not shown) a pronounced antiplasticizer effect is observed, which corresponds with the fact that  $T_g$  continuously increases as the picoline concentration is lowered; cf. Table I. Concerning the secondary relaxation, all properties typical of a JG process are found: Below  $T_g$  the relaxation strength  $\Delta\varepsilon_\beta$  only weakly depends on temperature, whereas the time constants closely follow an Arrhenius law; cf. Figs. 3 and 4:

$$\tau_\beta(T) = \tau_0 e^{\Delta H_a/k_B T}. \quad (1)$$

As is demonstrated in Table I and Fig. 3, there is a simple relation between the mean activation energy  $\Delta H_a$  and the glass transition temperature:  $\Delta H_a/k_B \approx 25T_g$ , with the only significant exception being the system with the lowest picoline concentration of 5%. This agrees well with what was previously reported for many different neat glass formers [5,7]. Thus, on the  $T_g/T$  scale different picoline concentrations are reflected only in a systematic variation of the preexponential factor  $\tau_0$ , which changes by about 5 orders of magnitude; cf. Fig. 3.

Figure 4 shows the time constants  $\tau_\beta$  as a function of temperature. The inset of Fig. 4 demonstrates that the mean activation energy  $\Delta H_a$  and the preexponential factor  $\log(\tau_0)$  are connected by a linear relation:

$$\Delta H_a/k_B = -T_{\text{iso}} \ln(\tau_0/\tau_{\text{iso}}). \quad (2)$$

This relation defines an isokinetic point at  $T_{\text{iso}} \approx 70$  K and  $\tau_{\text{iso}} \approx 10^{11}$  s for all binary mixtures investigated that contain 2-picoline as the smaller component, i.e., picoline

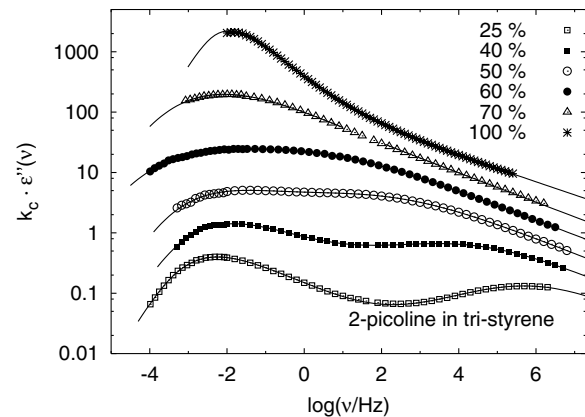


FIG. 2. The dielectric loss of different 2-picoline in tri-styrene mixtures with similar  $\alpha$  relaxation times, for clarity shifted by a concentration dependent prefactor  $k_c$ . Solid lines are interpolations using appropriate model functions [2,14].

TABLE I. Glass transition temperature  $T_g$ , mean activation energy  $\Delta H_a$ , and the prefactor  $\tau_0$  of the Arrhenius law for the 2-picoline in tri-styrene systems. The concentration of 2-picoline is given in percent by weight.

% picoline	5%	25%	40%	50%	60%	70%	80%	100%
$T_g$ [K]	220.2	185.2	167.5	156.3	149.2	142.5	138.6	132.7
$\Delta H_a/k_B T_g$	14.9	23.5	26.0	25.0	24.6	25.5	25.4	26.2
$\tau_0$ [s]	$3 \times 10^{-15}$	$3 \times 10^{-17}$	$5 \times 10^{-16}$	$10^{-13}$	$2 \times 10^{-12}$	$10^{-11}$	$6 \times 10^{-11}$	$9 \times 10^{-11}$

in tri-styrene, picoline in OS-1000, picoline in OS-2000, and picoline in *o*-terphenyl (*o*-TP); cf. the inset of Fig. 4. The solid lines in Fig. 4 (main part) represent Arrhenius laws, which fulfill Eq. (2). Thus, for all concentrations above 5%,  $\tau_\beta(T)$  may be represented as

$$\tau_\beta(T) = \tau_{\text{iso}} e^{-\Delta H_a/k_B T_{\text{iso}}} e^{\Delta H_a/k_B T}. \quad (3)$$

As the above equation is a common description for both the HF wing (high concentrations) and the  $\beta$  peak (low concentrations), one might already at that point conclude that the underlying relaxation process is identical. This conclusion is strongly supported when one investigates the evolution of the line shape of the secondary relaxation: In Fig. 5 the exponent  $\gamma$  of the HF power law of the secondary relaxation peak (low concentrations) and the HF wing (high concentrations) is shown as a function of temperature, and it is seen that, below the glass transition of each mixture,  $\gamma(T)$  falls onto a master curve for all concentrations investigated. Deviations from this master curve occur only around and above the respective  $T_g$  of each mixture. The dashed line in Fig. 5 represents the relation  $\gamma(T) \propto T$  that is expected for the simplest case of thermally activated dynamics [2]. Thus, there is one secondary process that, depending on the time scale ratio  $\tau_\alpha/\tau_\beta$ , appears either as a HF wing or a separate peak. In the glass the time constants of this process scale with  $T/T_g$ , whereas the exponent  $\gamma$ , which at the same time

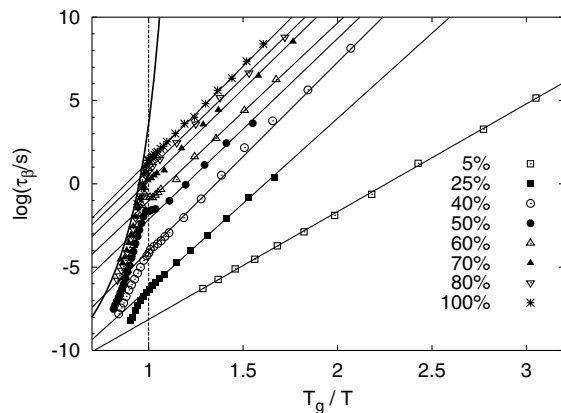


FIG. 3. The time constants of the secondary process in picoline/tri-styrene systems. Solid lines: Arrhenius law. For comparison:  $\alpha$  relaxation times of the 40% picoline in tri-styrene system (bold line).

characterizes the width of the  $\beta$  peak [2], is given by a common function of the absolute temperature.

As is seen in the inset of Fig. 4, in a reexamination of the data for a series of polyalcohols (glycerol, threitol, xylitol, and sorbitol [8]) the same relation Eq. (2) is recovered with  $T_{\text{iso}} = 105$  K and  $\tau_{\text{iso}} = 3 \times 10^{11}$  s. For various other type B systems (solid triangles), however,  $\Delta H_a$  and  $\tau_0$  are seemingly unrelated.

So far the secondary relaxation was considered only below  $T_g$ . When the temperature dependence of the  $\beta$  process is inspected at  $T > T_g$ , a strong increase in the relaxation strength  $\Delta \epsilon_\beta$  is observed as is typical of a JG relaxation. In addition, a pronounced change in the temperature dependence of  $\tau_\beta$  occurs around  $T_g$ . In Fig. 3 the time constants  $\tau_\beta$  reveal a crossover from a simple Arrhenius behavior to a much stronger temperature dependence above  $T_g$ . In the case of intermediate concentrations, e.g., in the system 40% picoline in tri-styrene, and at high enough temperatures  $\tau_\beta$  may be extracted by a simple determination of the peak frequency from the data. At higher concentrations the situation is different as main and secondary relaxation processes overlap strongly. However, by increasing the molecular weight of the oligo-styrene molecules both  $\alpha$  and  $\beta$  relaxation may again be separated. It turns out that the time constants

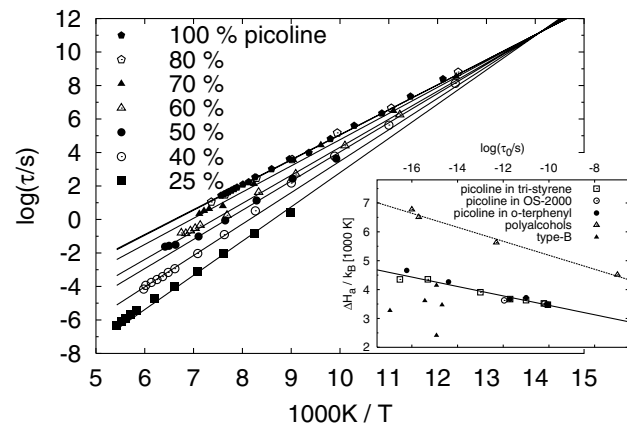


FIG. 4. The time constant  $\tau_\beta$  of the  $\beta$  process for different picoline in tri-styrene systems. The inset demonstrates the relationship between the activation energy  $\Delta H_a$  and the pre-exponential factor  $\tau_0$ , which exists for the binary mixtures studied here, but also for a class of polyalcohols discussed elsewhere [8]. Solid lines in main figure show Arrhenius laws according to Eq. (3).

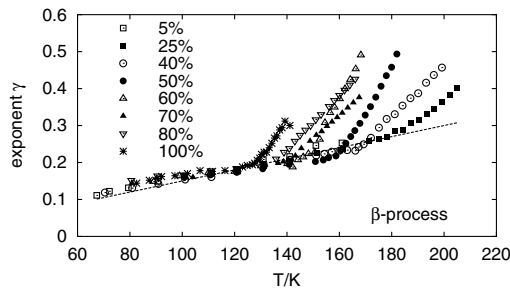


FIG. 5. Exponent  $\gamma$  of the high frequency power law of the  $\beta$  process as a function of temperature for various picoline/tri-styrene systems. Dashed line:  $\gamma \propto T$  as expected for thermally activated dynamics.

of the secondary process are basically unchanged by that procedure, so that  $\tau_\beta(T)$  may again be extracted unambiguously, even at higher concentrations and above  $T_g$ ; cf. Fig. 6. Similar deviations from the Arrhenius temperature dependence were reported recently for the polyalcohols sorbitol and xylitol [17]. In the latter work  $\alpha$  and  $\beta$  relaxation were separated by the application of pressure, and the observed crossover in  $\tau_\beta(T)$  was shown to be consistent with theoretical model considerations.

In summary, we have demonstrated that the relaxation process underlying the HF wing in neat picoline can be made fully visible when picoline is investigated in a mixture with oligo-styrene, as main and secondary (HF wing) processes become well separated in the low and intermediate concentration regimes. By combining frequency and time-domain spectroscopy and using a powerful phenomenological approach, time constants and line shape parameters were extracted, covering a sufficiently

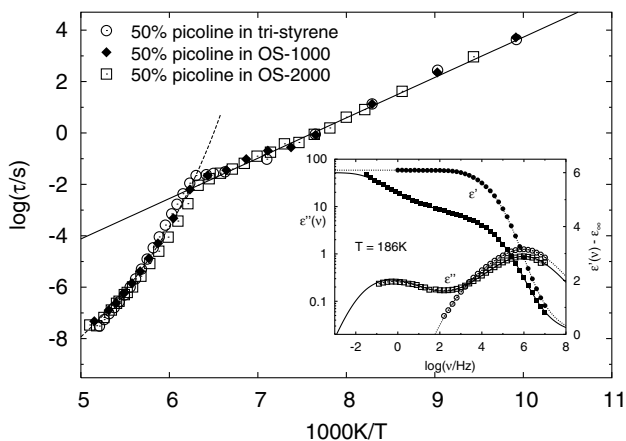


FIG. 6. The time constant  $\tau_\beta$  of the  $\beta$  process in systems with 50% picoline in different oligo-styrenes. Lines are a guide to the eye. The inset shows real (right axis) and imaginary parts (left axis) of the complex permittivity for two systems containing tri-styrene (circles) and OS-2000 (squares), both at  $T = 186$  K so that the stronger separation between  $\alpha$  and  $\beta$  relaxation may become obvious. Interpolations use model functions and the WW approach as explained in [2,14].

broad temperature range. In particular, concerning the secondary relaxation such an analysis indicates that at all concentrations the same relaxation process is observed and that it exhibits all features typical of a JG relaxation. The distinction between type *A* and type *B* behavior in the present systems turns out to be a matter of the time scale ratio of main and secondary relaxation, which is basically determined by the preexponential factor  $\tau_0$ . As the latter continuously covers a range of about five decades, type *A* might be called the limit for a secondary relaxation with particularly large  $\tau_0$ .

It was shown that the  $\beta$  process in the binary systems as well as in a homologous series of polyalcohols is well characterized by a respective isokinetic point. Whether it will be possible to fit the majority of type *B* systems into such a scheme of chemically related substance classes, however, has to remain an open question. Not yet clear is also how the two secondary processes that appear in systems where both HF wing and  $\beta$  peak are present (e.g., 3-fluoro aniline, phenyl glycidyl ether, tri methyl phosphate [18], 2-methyl tetrahydrofuran [19]) possibly fit into that picture. Maybe, in particular, light scattering (LS) experiments will be able to shed further light on this question, as recent studies indicate that the HF wing is detected in LS and DS alike [20], whereas a secondary relaxation peak has not yet been reported in LS measurements [21].

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