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The component dynamics of miscible binary mixtures of glass-formers: new features

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Abstract

Opposite effects on the width of the dispersion of the α-relaxation and the separation on the time scale of the Johari-Goldstein β-relaxation from the α-relaxation are predicted for guest molecules dissolved in a host depending on whether the glass transition temperature of the host is higher or lower than that of the guest. These predictions are tested by dielectric relaxation measurements on mixtures of two glass-forming mixtures. The results are in agreement with the predictions.

Keywords: dielectric relaxation; glass-forming liquids; secondary relaxation; binary mixures

1 Introduction

Explanation of the dynamics of a component in binary miscible mixtures found by experimental measurements has occupied the attention of the research community. Of interest is the change of the dynamics of a glass-former (the guest) when it is homogeneously mixed with another glass-former (the host). By now, it is well known that the guest and the host have their own individual dynamics in the mixture [1--6]. The most noticeable and easily observed change of the dynamics of the guest is that of its primary α-relaxation, including the shift of the α-relaxation time, $\tau_{\alpha,g}$, to either longer or shorter times depending on the composition of the mixture. This is the primary concern of most theoretical models of mixtures [7--9]. However, the focus of these models solely on the α-relaxation of a component may have left out an important aspect of the dynamics coming out to light in recent years. The aspect is the possible fundamental role played by secondary relaxation which has properties either mimicking or correlated with that of the α-relaxation in neat glass-formers. Some examples of experimental data showing the strong connection of the α-relaxation with secondary relaxation belonging to this special class, called Johari-Goldstein (JG) β-relaxation, are given in Refs.[10-14]. The connections imply that the α- and JG β-relaxations are inseparable processes in considering glass transition. Remarkably, the connection is passed onto the α- and JG β-relaxations of a component in mixtures of two van der Waals glass-formers. An example is the invariance of the ratio of $\tau_{\alpha g}$ to $\tau_{JG,g}$, the relaxation time of the JG β-relaxation, to widely different combinations of pressure and temperature that maintain $\tau_{\alpha,g}$ constant [15-16]. This is a remarkable result because in these experiments the specific volume varies over a significant range, and yet $\tau_{\alpha g}/\tau_{JG,g}$ is invariant at constant $\tau_{\alpha g}$. So far, there is only one

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published model of component dynamics in mixtures based on the Coupling Model (CM) that addresses both the α- and JG β-relaxations of a component, and can explain their various connections [6, 15-17]. In all mixtures considered thus far, the guest in its pure state has a lower glass transition temperature than that of the host. Therefore, in the mixture, replacement of guest molecules by the less mobile host molecules will stretch the α-relaxation process associated with the guest molecules to longer times. This heuristic description suggests increased stretching of the correlation function or equivalently broadening of the frequency dispersion of the guest component α-relaxation. Also, the less mobile host molecules enhance the intermolecular constraints on the motions of molecules participating in the guest component α-relaxation. From this, the CM expects the coupling parameter n_g of the guest molecule in the mixture to be larger than its value n_0 of the guest molecules in the pure state. Since the α-correlation functions of the guest in the mixture and in the pure state are given by $\phi(t) = \exp\{-(t/\tau_{\alpha g})^{1-n_g}\}$ and $\phi(t) = \exp\{-(t/\tau_{\alpha})^{1-n_0}\}$ respectively, from $n_g > n_0$ we expect the width of the guest molecules α-dispersion is increased when mixed with the host having higher T_g. As shown in Ref.[6] and will not be repeated here, the other prediction of the CM is on the separation between the α-relaxation and the JG β-relaxation. The separation, measured by the difference of the logarithm of their relaxation times, is given by

$$\log_{10}\tau_{\alpha} - \log_{10}\tau_{JG} = n_0(\log\tau_{\alpha} + 11.7) \quad (1)$$

for the pure guest, and

$$\log_{10}\tau_{\alpha g} - \log_{10}\tau_{JG,g} = n_g(\log\tau_{\alpha g} + 11.7) \quad (2)$$

for the guest in the mixture. Again, because of $n_g > n_0$, the separation is larger in the mixture if $\tau_{\alpha} = \tau_{\alpha g}$.

Several previous experimental studies [15, 16, 18-22] and simulations have verified two simultaneous CM predictions in mixtures where the host has a significantly *higher* T_g than the guest. They are:

(i) The frequency dispersion of the guest α-relaxation in the mixture is broader than the pure guest (besides the broadening by composition fluctuations in mixtures).

(ii) The JG β-relaxation is further separated from the α-relaxation in the mixture than in the pure guest.

The case of polar guest in apolar host is particularly interesting for dielectric spectroscopy, as the contribution to the overall loss spectrum is mainly due to to the dipoles of the guest molecules. Therefore, dielectric spectroscopy is probing selectively the orientational dynamics of the polar molecules. However, attention has not been given to the CM predictions for the reverse situation, i.e. when the apolar host has a *comparable* or *lower* Tg than the dipolar guest. In this opposite case, the more mobile host molecules mitigate the intermolecular constraints of molecular motions in the guest α-relaxation, and hence $n_g < n_0$. From this, we immediate make the two following predictions.

(iii) The frequency dispersion of the guest α-relaxation is narrower in the mixture than in the pure guest (not taking into account of the broadening by composition fluctuation in the mixture).

(iv) Since Eqs.(1) and (2) are general, now they predicts that the separation between the guest α-relaxation and the JG β-relaxation will decrease in the mixture.

The purpose of this paper is to critically test these simultaneous predictions by new analysis of previously obtained dielectric relaxation data of 10 wt.% dipolar benzylacetate (BzAc) with T_g=165.1 K in apolar host, isopropylbenzene (IPB) with T_g=128.5 K or *o*-terphenyl (OTP) with T_g=244 K [23]. The T_g of OTP is 80 degrees higher BzAc, while the T_g of IPB is slightly lower than BzAc. Test is also made by newly acquired dielectric relaxation data of dipolar bromoethylbenzene (BrEBz) with T_g=135.6 K in apolar host, ethylbenzene (EB) with T_g=115 K or tri-styrene (3S) with T_g=232 K.

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2 Experimental Section

The details for measurements on BzAc and mixtures with IPB and OTP can be found in Ref.[23--24]. Bromo-2-ethylbenzene (BrEBz), ethylbenzene (EB) were obtained from Aldrich and used as received. Tristyrene (3S) with molecular weight=370 g mol^{-1}, M_w/M_n=1, was obtained from Polymer Standard Service. All samples were stored and handled in dry nitrogen atmosphere. The polar molecules were dissolved in the apolar solvents at molar concentration of about X_M=0.1 for BrEBz and at weight fraction X_W=0.1 for BzAc (determined by mass balance). Dielectric measurements were carried out using a Novocontrol Alpha-Analyzer ($\nu=10^{-2}$-10^{7} Hz). The sample cell, made up by a parallel plate capacitor separated by a quartz spacer (geometric capacitance ~ 90 pF), was filled by the sample and placed in the nitrogen flow Quatro cryostat for temperature control.

3 Results and Discussion

3.1 BzAc and mixtures of BzAc in IPB or OTP (X_W=0.1)

In Figure 1 we present the isochronal dielectric loss at 1 kHz, ε"(1 kHz), of neat BzAc, 10 wt.% of BzAc in IPB, and 10 wt.% of BzAc in OTP. Spectra of the pure weakly polar solvents are also shown. In addition to the α-loss peak located near 175 K, the isochronal spectrum of neat BzAc shows a low temperature secondary relaxation γ-loss peak. As suggested from the molecular structure of BzAc shown in Fig.1, this γ-relaxation is likely coming from rotation of the –OOC-CH_3 unit at the flexible oxygen bond, which links it to the benzene ring. The intramolecular nature of γ-relaxation indicates that it is not the JG β-relaxation [11]. This will be supported by the insensitivity of the γ-relaxation time to mixing BzAc with OTP and IPB to be discussed shortly below. If the JG β-relaxation exists in neat BzAc, it must be located at temperatures in between the α- and the γ-relaxation, and hence unresolved.

On mixing 10 wt.% of BzAc with OTP having much higher T_g, it can seen from Fig.1 that the α-loss peak of BzAc is shifted to about 250 K while the location of the γ-loss peak remains practically unchanged. A new secondary β-relaxation of BzAc now appears in the isochronal spectrum. This must be the JG β-relaxation of BzAc in the mixture with OTP. It is now resolved because of the JG β-relaxation of BzAc is further separated from the α-relaxation of BzAc in the mixture according to prediction (*ii*).This process comes from the contribution of dipole fluctuations of BzAc molecules coupled to the motions of the overall system (i.e. mixture OTP/BzAc) in the glassy state. In this sense, the relaxation is truly intermolecular in nature. Its amplitude, frequency and temperature behavior may depend on the characteristics of the apolar solvent but also on those of the dipolar probe, as clearly shown for different halogenated benzenes in ref.[23].

In the mixture of 10 wt.% of BzAc with IPB, the guest BzAc α-loss peak is shifted by approximately 25 degrees to lower temperatures, reflecting the neat host IPB having a lower T_g than the neat guest. The location of the γ-loss peak is practically unchanged. As a result, the α- and the γ-relaxations of BZAc in the mixture get closer together than in pure BzAc. This together with the prediction (*iv*) make the JG β-relaxation of BzAc in the mixture with IPB even harder to resolve than in pure BzAc.

Isothermal loss spectra, ε"(f/f_{max}), emphasizing only the contribution from the α-relaxation are shown in Fig.2 for pure BzAc, 10 wt.% BzAc in mixtures with OTP and with IPB. Several sets of data taken at different temperatures and f_{max} centered about 1 kHz are shown for the α-relaxation of BzAc in 10 wt.% BzAc mixtures with OTP. These isothermal loss data were taken by spectrometer that has a narrow frequency range [23], and the JG β-relaxation of BzAc found in this mixture at much higher frequencies cannot be displayed together

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with the α-relaxation at these temperatures. It can be seen from Fig.2 that its frequency dispersion is much broader than that of pure BzAc, consistent with prediction (*i*). On the other hand, the frequency dispersion of the BzAc α-relaxation in the mixture with IPB is almost the same as that of pure BzAc. Interestingly, the log-log slope of the high frequency flank of the α-peak in the mixture is steeper than in the case of pure BzAc. The possible effect of broadening due to the contribution of the secondary relaxation has o be excluded in this case: in fact the data reported in Fig.2 are obtained by using a master curve procedure, i.e. by shifting several spectra obtained at different temperatures and normalizing their intensity and their frequency to that of the loss peak maximum. Therefore, as the different spectra superpose well in the master curve, the effect of the seconday relaxation is negligible, otherwise the shape of the spectra should change with temperature, as the α-β separation and their mutual contribution change on cooling. Although the concentration of BzAc in the mixture of 10 wt.% of BzAc with IPB is not large, presence of some residual composition fluctuations and broadening of the α-relaxation cannot be excluded. Taking this effect into account and the fact that the T_g of IPB is not much lower than that of BzAc, the data seem to support the intrinsic narrowing of the α-dispersion of BzAc predicted by (*iii*).

3.2 BrEBz and mixtures of BrEBz in EB or 3S (X_M=0.1)

The new data of pure bromoethylbenzene (BrEBz), and mixtures of molar fraction X_M = 0.1 of BrEBz in ethylbenzene (EB) and in tri-styrene (3S) were taken by broadband spectroscopy. The isochronal dielectric loss spectra of these three samples at 1 kHz, ε"(1 kHz), are presented in Fig.3. In contrast to BzAc, the JG β-relaxation is already resolved in pure BrEBz both isochronically (see Fig.3) and isothermally (data not shown). In the mixture with 3S having a much higher T_g, the JG β-loss peak of BrEBz becomes more prominent compared with the neat BrEBz α-relaxation and further separated from the BrEBz α-loss peak. This is consistent with prediction (*ii*). On the other hand, in the mixture with EB having a lower T_g, the JG β-loss peak of BrEBz is suppressed, moved closer to the α-loss peak, and no longer resolved in the isochronal spectrum, in accordance with prediction (*iv*).

Isothermal loss spectra, ε"(*f*), of pure BrEBz, mixtures of BrEBz in ethylbenzene (EB) and in tri-styrene (3S) (X_M=0.1) all having approximately the same peak frequency are compared in Fig.4. The loss spectrum of pure BrEBz shows once more the resolved JG β-relaxation (seen as the shoulder in Fig.4, and resolved peaks at lower temperatures). In the mixture with 3S, the JG β-relaxation of BrEBz at the temperature shown in Fig.4 is located at frequencies much higher than the upper limit of the experimental frequency window. Its presence is assured in isothermal spectra taken at lower temperatures (not shown). It is clear from Fig.4 that the frequency dispersion of the α-relaxation of BrEBz is much broader in the mixture with 3S than in the pure state. This is in accord with prediction (*i*). While in mixture with EB, the α-loss peak of BrEBz is narrower than that of pure BrEBz on the high frequency flank, and an excess wing appears instead of the shoulder.

In Fig.4, also the contribution of the fitting function for α- and β- process is reported for the systems BrEBz and BrEBz mixed with EB, clearly showing that the α-peak is slighly narrower in the pure system than in the lower T_g mixture. We used for fitting a simple superposition of the two processes, usually performed in literature but arbirtary and strongly questionable, since the two processes are interrelated as shown in ref.[12, 15, 16]. Of course, when two processes are so close each other, no unequivocal procedure of deconvoluton is possible; but it is clear that any estimation of the true broadness of the α-peak should result in a narrower (or at least equal) shape than that of the convoluted peaks. Additionally, the contribution of the β-peak is not vanishing in the mixed system (the relative dielectric strength $\Delta\varepsilon_\beta/\Delta\varepsilon_\alpha$ is ~0.06 and 0.04 for the pure and

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mixed system, respectively): the narrowing of the α-peak in the mixture of BrEBz with EB cannot be ascribed to the vanishing of the secondary process.

Again, taking into account of residual spatially heterogeneous broadening by composition fluctuations in the mixture and the fact that the T_g of EB is only 20 K lower than BrEBz, the intrinsic narrowing of the α-relaxation of BrEBz predicted by (*iii*) accompanied by the decrease in separation between the α- and JG β-relaxations are consistent with observation.

A comparison of the results of §3.1-3.2 with the literature data for dynamics of guest molecules in host systems with different mobility is interesting. Almost four decades ago pioneering works [25--29] on dielectric spectroscopy of polar guest molecules in apolar hosts (with both lower and higher T_g than guest systems) gave evidence of pronounced changes of the breadth of the relaxation, mainly interpreted as effect of fluctuation concentration, but also of the emergence of the JG β-relaxation that was better evidenced [27--28] in mixtures with hosts with higher viscosity. A picture was proposed to explain the dielectric relaxation in solutions of rigid polar molecules in nonpolar solvents, based on the effect of viscoelastic relaxation of the solvent on the reorientation of the guest dipole under the applied electric field [29]: the breadth of distribution of relaxation times in the dielectric loss spectrum would be directly related to the steady-flow viscosity of the solvent, resulting in narrow and broad peaks for solvent with low and high viscosity, respectively. This picture is in agreement with CM preditcions. Recently, the probe rotation dynamics of probe polar molecules in viscous liquids has been studied [30] by dielectric spectroscopy as a function of the the size of the probe molecule relative to the liquid constituents. The change of the breadth of the α-relaxation was interpreted in terms of averaging the eniromental fluctuations due to heterogeneous dynamics. Bigger the size, higher is the degree of averaging, and the heterogeneous dynamics seen by the probe is averaged to result in a process with a very small distribution of time up to reach, for the hydrodynamic regime, a Debye-like relaxation. On the other hand, for size of the solute comparable to that of the solvent, a similar dispersion as that shown by the pure solvent is reported. Unfortunately in ref. [30] no experiments with solute of smaller size or with lower T_g than the solvent were reported. In these cases, as reported in our experiments, structural relaxation becomes very broad, with a distribution of relaxation time sometime exceeding that of the pure apolar solvent (see for instance BrEBz in 3S (Fig.4), with FWHM≈2.78, where for pure 3S FWHM≈1.9). Although the latter results cannot be explain by using the concept of heterogeneous dynamics as presented in [30], they are naturally explained by coupling model. The overall scenario is confirmed by studies of rotational motion of probe molecules in various hosts with different viscosity by time-resolved optical spectroscopy [31], for which the agreement with CM predictions has been tested [32].

4 Conclusion

Coupling model predicts the effects on the breadth of the α-relaxation and the separation between the α- and JG β-relaxation times of a guest glass-former by mixing with host glass-former are very different depending on whether the mobility (T_g) of the guest molecules is higher (lower) than that of the host molecules. While the case of T_g of the guest mobility being lower than the host had been studied in many systems by experiments and molecular dynamics simulation and the CM predictions tested, studies in the opposite case, when T_g of the guest is higher than the host, are quite rare and a comparison with CM predictions was never done. Our experimental data on two such mixtures have shown opposite directions of changes in the breadth of the α-relaxation and the separation between the α- and JG β-relaxation times of the guest glass-former by mixing with host glass-formers having lower and higher T_gs, in agreement with theoretical predictions.

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Figure Captions

Figure 1. Logarithm of dielectric losses at 1 kHz versus temperature for butylacetate: pure (dashed line), mixed with IPB (blue filled stars), mixed with OTP (red filled circles). Also the dielectric losses at 1 kHz of pure IPB (blue open stars) and OTP (red open circles) are shown or comparison. Inset shows the molecular structure of benzylacetate.

Figure 2. Bilogarithmic plot of dielectric losses versus frequency for benzylacetate. Data related to different temperatures have been shifted to obtain master curves, normalizing the intensity and the frequency to that of the loss peak maximum. Continuous line indicates the relaxation peak for pure benzylacetate, as obtained from previously reported fitting parameters [24]. Solid and open symbols indicate data of mixture in OTP and IPB, respectively.

Figure 3. Logarithm of dielectric losses at 1 Hz versus temperature for BrEBz: pure (open circles) and mixed with EB (full squares) and with 3S (full triangles). Data for pure EB (solvent) are shown as open squares. Lines are guides for eyes.

Figure 4. Bilogarithmic plot of dielectric losses, normalized to the peak maximum, versus frequency for pure BrEBz at 144.15 K (open circles), for the mixture BrEBz/EB at 125.15 K (full circles), for the mixture BrEBz/3S at 230.15 K (full stars). Lines are for fitting functions: solid lines represent the overall fits, dashed lines the Havriliak Negami functions for α-relaxation and dotted lines the Cole-Cole functions for β--relaxation.

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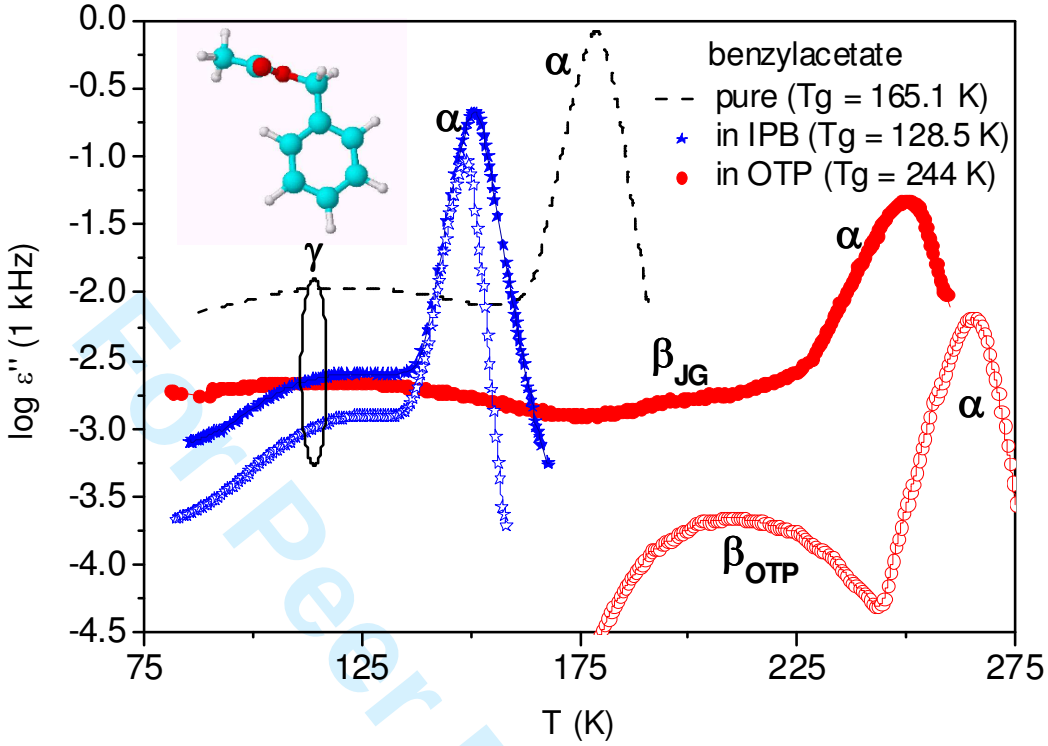

Figure 1

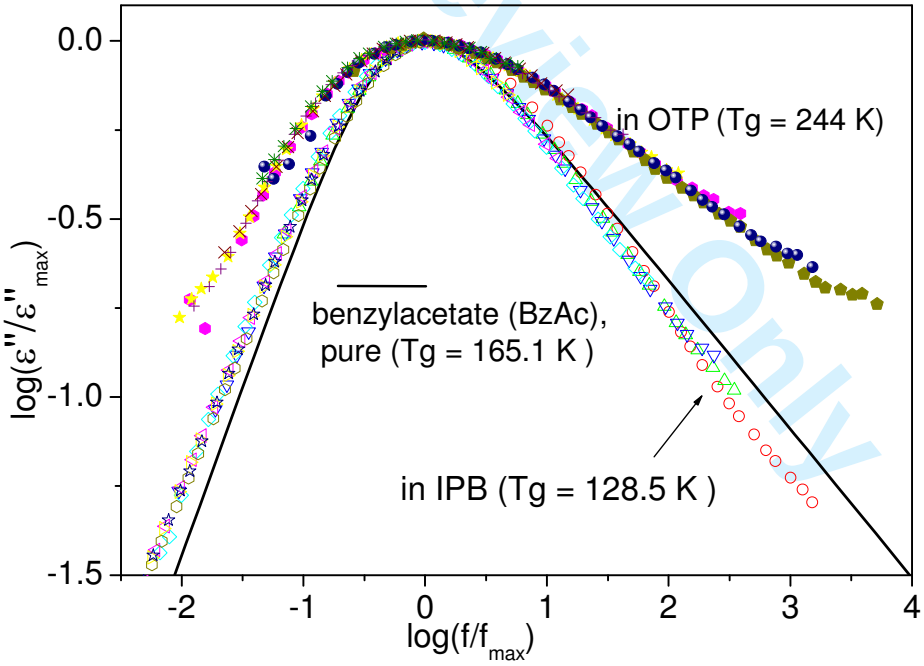

Figure 2

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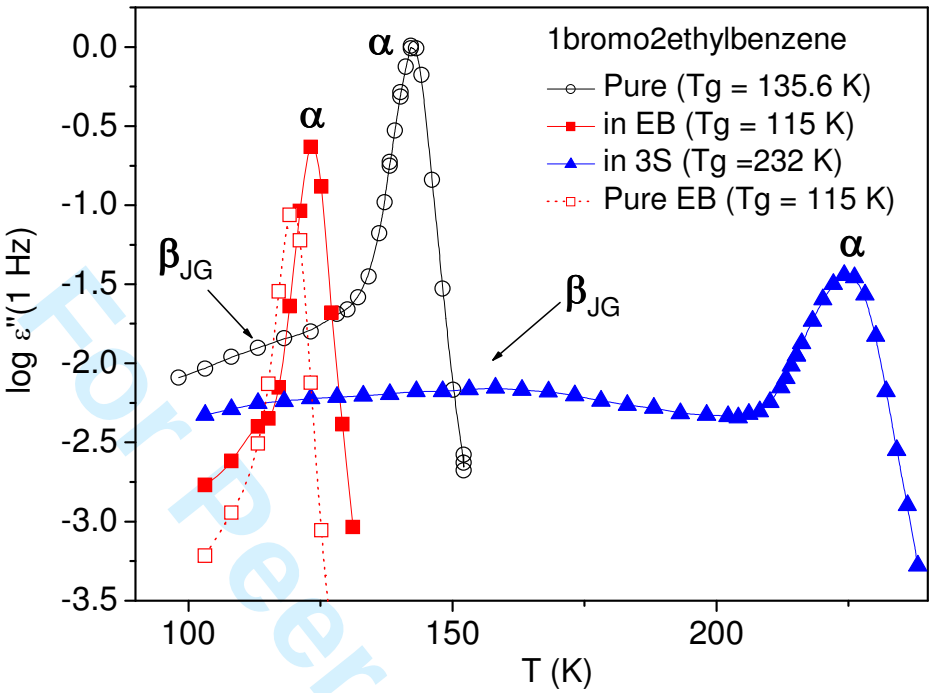

Figure 3

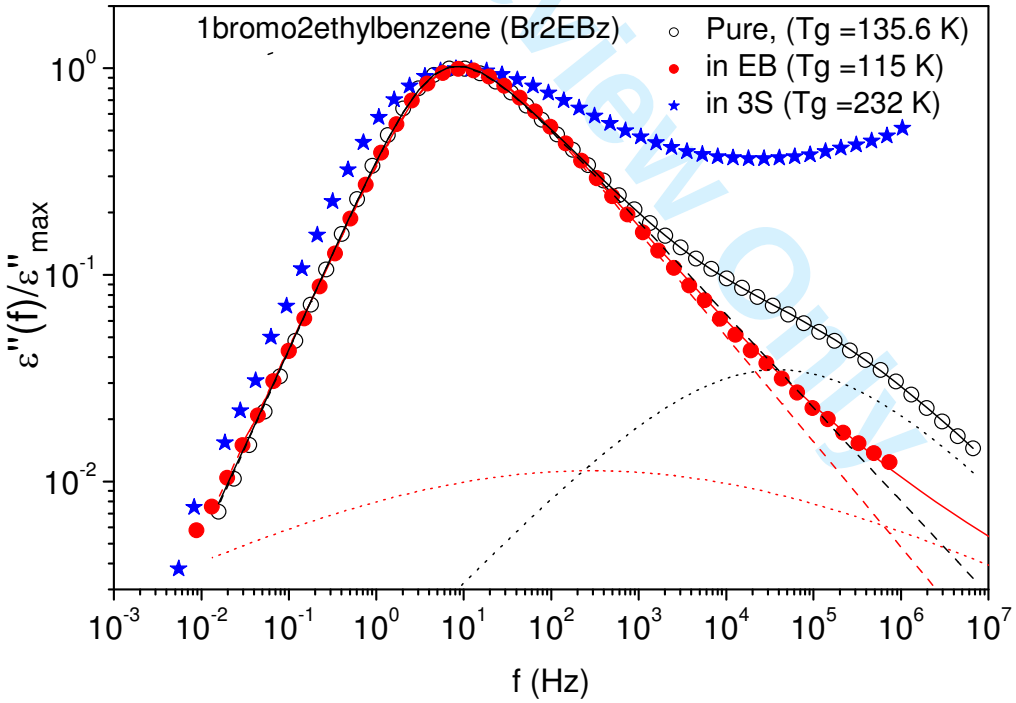

Figure 4

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