

The dielectric signature of glass density

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Abstract

At present, we are witnessing a renewed interest in the properties of densified glasses, prepared by isobaric cooling of a liquid at elevated pressure. As high-pressure densification emerges as a promising approach in the development of glasses with customized features; understanding and controlling their unique properties represents a contemporary scientific and technological goal. The results presented herein, indicate that the applied high-pressure preparation route leads to a glassy state with higher density (~1%) and a reduced free volume of about 7%. We show that these subtle structural changes remarkably influence the dielectric response and spectral features of β -relaxation in etoricoxib glass. Our study, combining dynamical and structural techniques, reveal that β -relaxation in etoricoxib is extremely sensitive to the variations in molecular packing and can be used to probe the changes in glass density. Such connection is technologically relevant and may advance further progress in the field.

Key words: densified glasses, secondary relaxation, dielectric spectroscopy

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The glass industry nowadays is a constantly growing market with a wide range of productive activities. Since the quality of these products depend on the structure of the glassy materials, much effort has been directed into creating glass with desired properties with respect to different technological purposes.¹ The unique non-equilibrium nature of the glassy state makes it very sensitive to preparation conditions and subsequent thermal treatment.² For instance, the technologically relevant high-density glassy state can be achieved *via* different ways i.e. by very slow cooling of a supercooled liquid, isothermal glass annealing (physical aging) or much more efficiently through layer-by-layer formation during vapor deposition procedure.^{3,4,5,6} Isothermal compression constitutes an alternative approach to transform a viscous liquid into the glassy state. Using hydrostatic pressure as another experimental variable allows one to approach a glass transition through different thermodynamic trajectories in T-p space leading to different glassy states.⁷

In this Letter, we investigated the secondary β -relaxation in etoricoxib glasses prepared *via* two different thermodynamic paths. The applied preparation protocols involve different temperature and pressure treatment as is schematically illustrated on V-T phase diagram in Figure 1. The first preparation route involved the conventional melt cooling procedure under ambient pressure (path A). The second preparation route, path B, assumed the glass formation by isothermal compression (at $T_2 = 398$ K which is 70 K above T_g) of the supercooled liquid to $p = 400$ MPa followed by isobaric cooling and release of pressure at room temperature ($T_1 = 293$ K). Path A yielded the ordinary glass (OG) while path B produced a new glassy state being described as densified glass (DG). At this point it is relevant to ask *how the preparation route will affect the properties of the resulting glass*. The concept of densified glasses is not new in glassy science. It has been established that high pressure impacts the dynamics, density and mechanical properties of a glass.^{8,9,10,11,12} The progress that has been done since the pioneering work of Weitz and Wunderlich⁸ allows one to assume that we can expect substantial differences in the features of OG and DG glasses. Thus, the previously asked question can be reformulated: *'to what extent the unique properties of DG glass can be probed by its dielectric response'*. To resolve this issue, we performed broadband dielectric spectroscopy (BDS) measurements at $p = 0.1$ MPa for OG and DG samples. The experimental details are presented in the supplementary material section. Our studies revealed an astonishing fact that secondary relaxation may constitute an extremely sensitive probe of molecular packing. In dielectric measurements we investigate the behavior of

permanent dipoles subjected to external electric field. When the electric field is removed the dipoles relax to their initial random positions. This process is not instantaneous. The time required for dipoles rearrangement in viscous medium is called relaxation time.¹³ The rate of relaxation depends on rotational freedom of molecules which successively is affected by temperature, local environment and proximity of neighboring molecules.¹⁴ Here, we observed that pressure densification of our material by about 1% significantly impacted the secondary relaxation behavior. To support our findings and discover the structural features behind the analyzed changes in dynamics, the degree of densification was quantified using the wide-angle X-ray scattering (WAXS) method and positron annihilation lifetime spectroscopy (PALS).

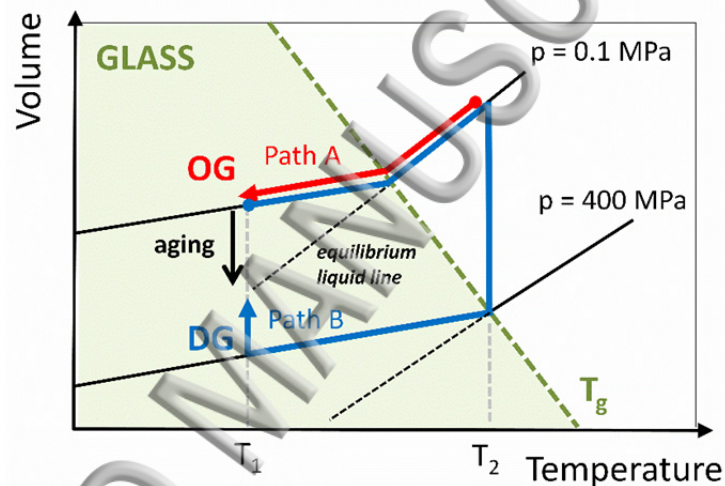


Figure 1. Schematic illustration of thermodynamic paths leading to various glassy structures (OG - ordinary glass, DG - pressure densified glass).

In our study we used etoricoxib drug as a model compound. Our choice was dictated by the desired features of its dielectric response, in particular the presence of a well-resolved and pressure-sensitive secondary relaxation. The utility of high-density glass as active pharmaceutical ingredients is intriguing in theory but in fact completely unexplored. The high-energy of densified materials is exceptionally attractive regarding the potential improvement of biopharmaceutical features (i.e. higher solubility), however, the lack of physical stability of such systems may be an insurmountable barrier during the practical implementation. Although the technological relevance of densified etoricoxib is not straightforward in fields other than pharmacology, the concept discussed in manuscript, of applying pressure to produce glass with

able structure and unique functionality unattainable using conventional ambient pressure processing, has been recognized in various fields including electrochemistry¹⁵ and aerospace industry¹⁶. Figure 2A shows the dielectric loss spectrum of OG at $T = 293$ K ($T_g = 328$ K)¹⁷. The dielectric spectra registered for increasing hydrostatic pressures at $T = 273$ K are presented in Figure 2B. It can be seen that upon compression the β -relaxation time, τ_β , gets longer and its amplitude gradually decreases. The observed shifting of β -process during compression can be quantified in terms of the activation volume law.¹⁸ The resultant value of activation volume $\Delta V = 29.8$ cm³/mol indicates that τ_β is sensitive to the reduction of intermolecular distances during compression.

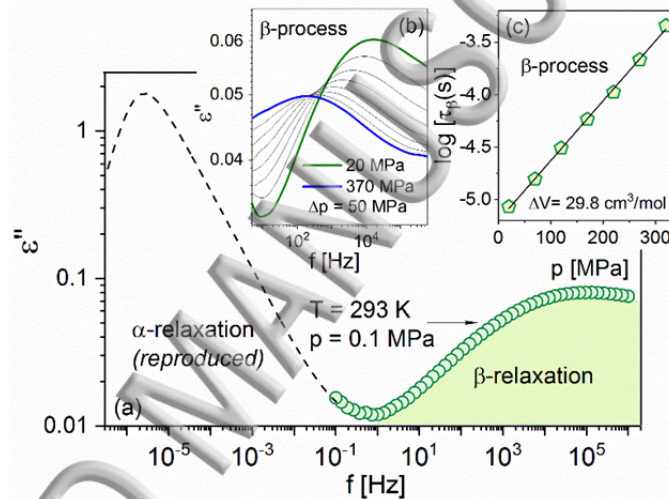


Figure 2. (a) The dielectric loss spectrum of etoricoxib (OG sample) registered at $T = 293$ K at atmospheric pressure. Green circles denote experimental data points. The position of structural relaxation peak was simulated from the data shifting. (b) Dielectric loss spectra measured for etoricoxib at various pressures at $T = 273$ K. (c) The pressure dependence of τ_β .

To further support this statement, it is valuable to disentangle the relative contributions of temperature and pressure to the observed τ_β behavior. Resolving this issue requires, however, measurements beyond the standard conditions. The ordinary way to distinguish whether volume or temperature are the overwhelming dynamics controlling parameters is to determine the ratio of apparent activation energy at constant volume to that at constant pressure, i.e. the E_v/E_p value.¹⁹ There are plenty of reports addressing this problem for structural relaxation in supercooled liquids.^{20, 21, 22, 19} Here, we make an attempt to estimate the E_v/E_p value for the

secondary relaxation dynamics. To do this the β -relaxation times were determined from dielectric measurements as a function of temperature and pressure, and pressure-volume-temperature (pVT) measurements had to be carried out in order to deduce the volume dependence of τ_β . We coupled β -relaxation times measured under isobaric ($p = 0.1$ MPa) and isothermal ($T = 273.15$ K) conditions using fitting parameters of the Tait equation describing pVT data below T_g (see Figure 3). Then, the E_v/E_p ratio was calculated according to the following formula:

$$E_v/E_p = \left[\frac{\partial \ln \tau_\beta}{\partial (T^{-1})} \right]_V / \left[\frac{\partial \ln \tau_\beta}{\partial (T^{-1})} \right]_p.$$

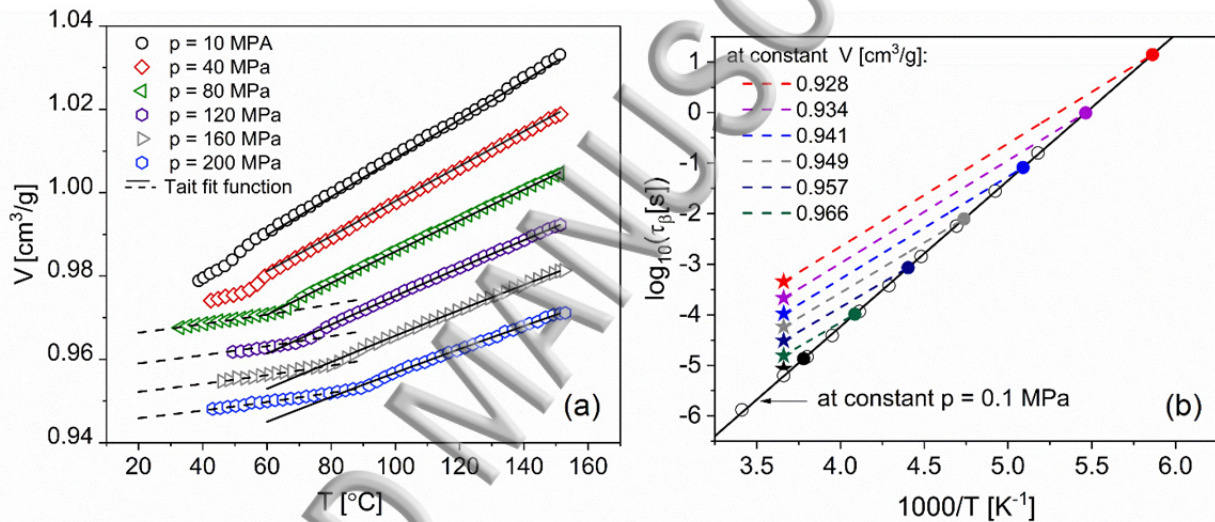


Figure 3. (a) Temperature dependence of the specific volume for various isobars. (b) Temperature dependence of β -relaxation times at constant pressure (open circles) and at constant volume (dashed lines).

From the data presented in Figure 3 we obtained the E_v/E_p ratios within the range of 0.71- 0.67. It is accepted that the closer to unity the E_v/E_p ratio is the greater the impact of thermal fluctuations on the relaxation dynamics. The obtained results confirm that temperature dominates over density in driving the β -relaxation dynamics in the OG sample but the effect of density cannot be neglected. What is interesting we observe that the E_v/E_p ratios for structural and secondary relaxation dynamics are quite similar. The E_v/E_p value calculated for the α -relaxation process was $E_v/E_p = 0.57$ ($T = 339$ K) (see supplementary information). This shows that secondary relaxation “mimics” the behavior of the α -relaxation process. This kind of behavior is usually

attributed to the secondary relaxations being described as a Johari-Goldstein (JG) type.^{23,24} It is consistent with results presented by Romanini et al. for ternidazole drug. They showed that α and JG β -relaxation times fulfil the density-dependent thermodynamic scaling and can be scaled using the same scaling exponent.²⁵ Among features typically assigned to secondary JG-relaxations the agreement between the JG-relaxation time and the primitive relaxation time of the Coupling Model is usually indicated.^{26,27} For etoricoxib this relation is not fulfilled and its classification as JG-process is not straightforward. To shed more light on the molecular origin of the β -process we performed theoretical calculations in the framework of density functional theory (DFT/B3LYP²⁸ method with G3 dispersion²⁹ correction and TZVP basis set³⁰) using Gaussian09 program³¹. We simulated the following rotations: (1) phenyl-CH₃, (2) pyridine-SOCH₂, and calculated the corresponding energy barriers, which were 18.0 kJ/mol and 36.3 kJ/mol, respectively. The changes in energy and dipole moment associated with these conformational interconversions are presented in supplementary information. By comparing the theoretical and experimental values determined in our previous studies¹⁷ (which was 53 kJ/mol) we deduced that the analyzed β -process may be associated with the rotation of the phenyl ring with the methyl sulfone group attached. It seems highly reasonable that rotations of such large molecular fragment will be sensitive to the environment and molecular packing. Considering this we classified β -process in etoricoxib molecule as a pseudo-JG relaxation.

It is well established that liquids subjected to cooling at elevated pressure and subsequently decompressed lead to glassy states of higher density when compared to those vitrified at atmospheric pressure.³² Our goal is to resolve whether such differences might be probed in detail by secondary relaxations within the course of dielectric measurements. The dielectric loss spectra for OG and DG samples detected at atmospheric pressure and at $T = 293$ K are compared in Figure 4a. We observed that the β -process in DG sample is narrower, has lower amplitude and moves nearly $\Delta f = 0.4$ decade towards the low frequency side in comparison to the β -process in the OG sample. Within the investigated temperature range the relaxation times τ_β for the DG sample proved to be longer than that observed for the OG glass. The temperature dependence of τ_β obeys the Arrhenius activation law (see Figure 4b), $\tau_\beta = \tau_0 \exp(E_a/RT)$, with the activation energy slightly higher for the DG sample (DG: $E_a = 58.25$ kJ/mol \pm 0.30, $\log \tau_0 = -16.04$ s, and OG: $E_a = 54.74$ kJ/mol \pm 0.41, $\log \tau_0 = -15.65$ s). Our dielectric data revealed that the preparation route incorporating pressure led to the formation of dynamically less heterogeneous glassy state

as indicated by narrower distribution of β -relaxation times in DG sample. The more efficiently packed structure in the DG sample led to the slowing down of its secondary relaxation dynamics. The only non-intuitive feature is a drop of amplitude of the β -process in the DG sample opposite to those expected for denser glassy state. However, such counter-intuitive behavior is sometimes observed in dielectric studies.^{33,34} For instance, the drop of amplitude was observed for the OG sample subjected to increasing pressure, or, is commonly observed during the physical aging when glass relaxes towards the equilibrium liquid state.³⁵

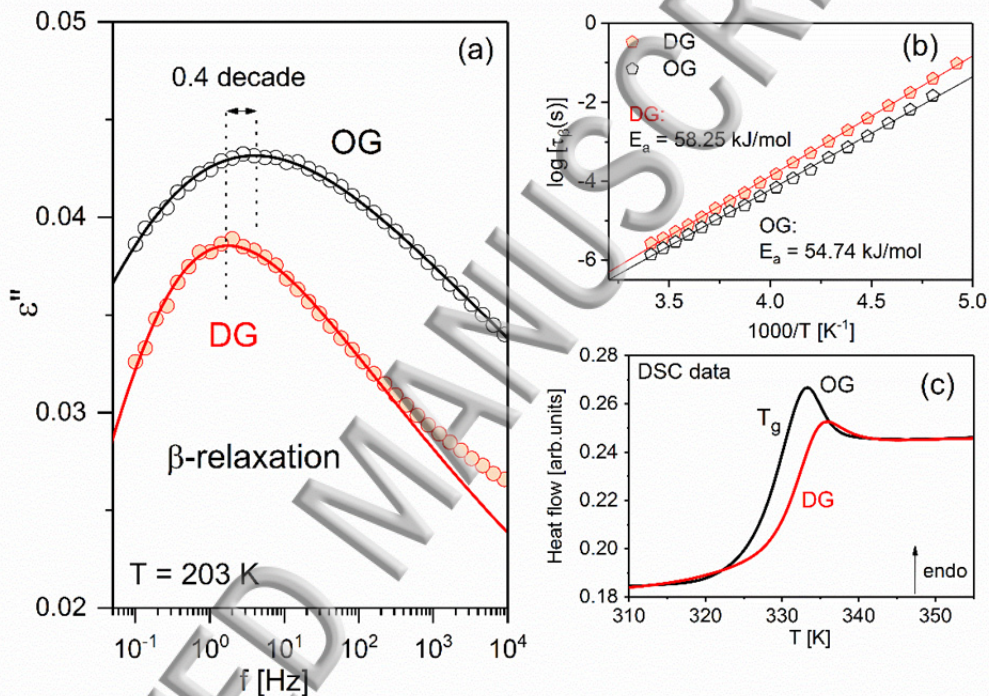


Figure 4. (a) The comparison of dielectric loss spectra registered at $T = 203$ K for OG and DG samples. Solid lines represent Havriliak-Negami fit functions. (b) The temperature dependence of relaxation times for both samples. (c) DSC traces obtained during heating of glassy etoricoxib with heating rate equals to 10 K/min. The solid black and red lines show the behavior of OG and DG glasses, respectively.

Now it seems relevant to ask how sensitive the secondary β -relaxation in etoricoxib to changes in molecular packing is. To verify this, we have to find out to which extent the applied high-pressure preparation route impacts the molecular packing of the etoricoxib glass. To get insight into the atomic rearrangements we probed the averaged atomic structure of DG and OG glasses

using the wide-angle X-ray scattering (WAXS) method. The total measured structure factor $S(Q)$ can be expressed as the sum of the molecular form factor associated with the intramolecular structure and the molecular packing structure factor related to intermolecular correlations. In Figure 5 the first diffraction peak appearing at about 1.45 \AA^{-1} can be attributed to the intermolecular interactions, since the intramolecular part gives only a weak contribution to the main diffraction peak at around 1.95 \AA^{-1} . In the inset of Figure 5, the zoom of the first diffraction peak clearly shows a slight shift for the DG sample to larger Q values when compared with the OG sample. It corresponds directly to a decrease in the intermolecular distances and indicates a more compacted structure of the DG. The position of the first diffraction peaks in the studied glasses is related to the intermediate-range order of the structure with the correlation length $L = 2\pi/Q_L$, where Q_L is the position of the peak maximum. Assuming that the volume of the etoricoxib glasses is proportional to the L^3 one can simply estimate the relative increase in the density of the DG to be approximately 1% in comparison with the OG.

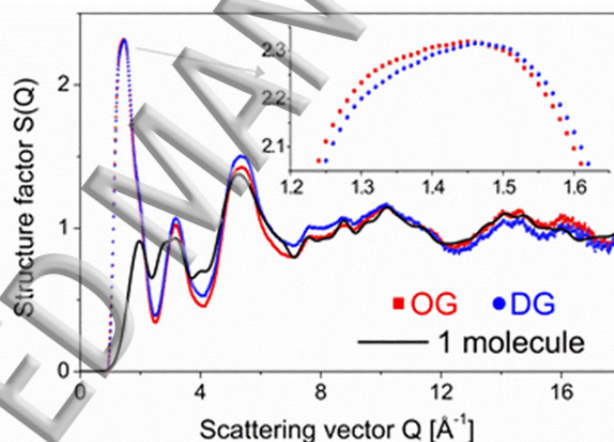


Figure 5. The representation of the X-ray diffraction data for the OG and DG glasses. The theoretical structure factor for a single etoricoxib molecule was shown for comparison (black line).

The differences in molecular packing of OG and DG samples were further analyzed using positron annihilation lifetime spectroscopy (PALS). The lifetime of *ortho*-positronium (*o*-Ps) annihilating inside the voids or holes in the investigated glass corresponds to the average size of unoccupied volume and is also sensitive to enhanced packing.³⁶ The microscopic free-volume

properties for DG and OG samples are presented in Table 1. Inside the free volumes of the more or less packed amorphous structures the high-energy positrons undergo annihilation in different ways giving contribution to a particular component of measured life time.¹¹ The key is the third, the long life-time component of applied fitting function which is connected with the formation of positronium in the free volumes of the investigated material. We found that the *o*-Ps lifetime τ_p was calculated as $\tau_p^{\text{DG}} = 1.456$ ns and $\tau_p^{\text{OG}} = 1.493$ ns. This corresponds to the following average free volumes $V_{\text{free}}^{\text{DG}} = 0.063$ nm³ and $V_{\text{free}}^{\text{OG}} = 0.068$ nm³ for DG and OG samples, respectively. This means that the average free volume in the DG glass is about 7% smaller in comparison to the OG.

Table 1. Data from the PALS experiment for DG and OG glasses. The τ_{free} , τ_{trapp} and τ_p are a particular component of measured life time (details are in supplementary information). The σ denotes the width of the values distribution, while I_{free} , I_{trapp} and I_p are the intensities of the components.

sample	τ_{free} [ns]	τ_{trapp} [ns]	$\sigma_{\tau(\text{trapp})}$	τ_p [ns]	$\sigma_{\tau(p)}$	V_{mean} [nm ³]	$\sigma_{V\text{mean}}$	I_{free}	I_{trapp}	I_p
DG	0.2148	0.3804	0.137	1.456 (17)	0.488	0.063	0.0546	22.474	51.907	25.618
OG	(21)	(47)	(31)	1.493 (17)	(7)	0.068	0.0556	22.450	51.261	26.290

The results presented herein indicate that the applied high-pressure path led to the glassy state with higher density (~1%) and a reduced free volume of about 7%. Similar findings were presented for polymers where the changes in overall specific volume in pressurized polymers are caused only by changes in free volume, while the occupied volume remains independent on processing history.^{37, 38} These subtle structural changes remarkably influence the spectral features of β -relaxation in etoricoxib glass. This shows that this pseudo-JG relaxation behaves like a density indicator and is extremely sensitive to variations in molecular packing. Such connection between the glassy structure and dynamical response is technologically relevant due to the actual need to produce glasses with customizable features with respect to different technological applications. In light of the growing interest in densified glasses and still limited understanding of their properties, dielectric spectroscopy may help to establish and understand their

extraordinary features. However, some limitations should be also pointed out here. One can notice that the dielectric features found herein for the DG sample are very similar to those reported for vapor deposited glasses⁴. This can lead to certain misinterpretation. In both cases we are dealing with glassy states of high-density being, however, totally different in terms of local order and energy configuration. During the procedure of glass vapor deposition the material tends to approach the low-entropy, enthalpy, and volume state of its equilibrium liquid state. Due to the lower position in the energy landscape (lower enthalpy) achieved during the growth procedure a prominent heat capacity overshoot during transition to the liquid state is a characteristic feature of vapor deposited glasses.³ The pressure densified glasses behave in an opposite way. During densification under high pressure the energy becomes locked in a compressing material leading to the highly energetic glassy state. This excess energy is retained as long as mobility of molecules are “frozen” in a glassy state. The increase of temperature allows for volume relaxation and releases the accumulated energy. Thus, the nature of enthalpy overshoot in DG glasses is different from those observed for the OG sample (see Figure 4c). Despite this limitation our results, focusing both on dynamical and structural features of densified glass, revealed that from the analysis of secondary relaxation dynamics during dielectric studies some useful information about the structure (density) of glass can be obtain.

SUPPLEMENTARY MATERIAL

See supplementary materials for more experimental details. The details of pVT analysis and results of thermodynamic scaling for α -relaxation process are included (i.e. master curve obtained when $\log\tau_\alpha$ is plotted against the thermodynamic quantity $1/TV^\gamma$, E_v/E_p ratio). Energy and dipole moment fluctuations during the rotation of certain side groups in the etoricoxib molecule determined from DFT simulations for a single molecule are shown.

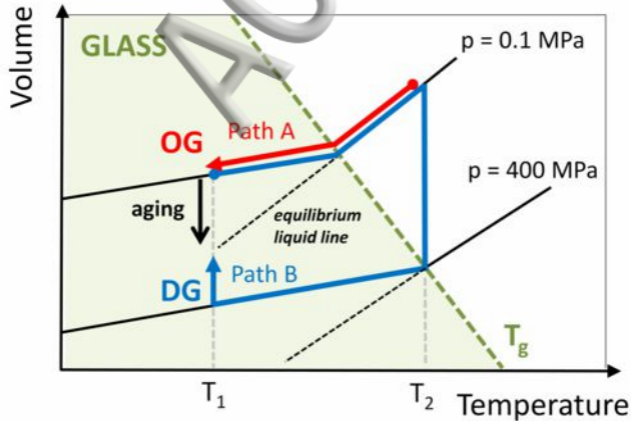
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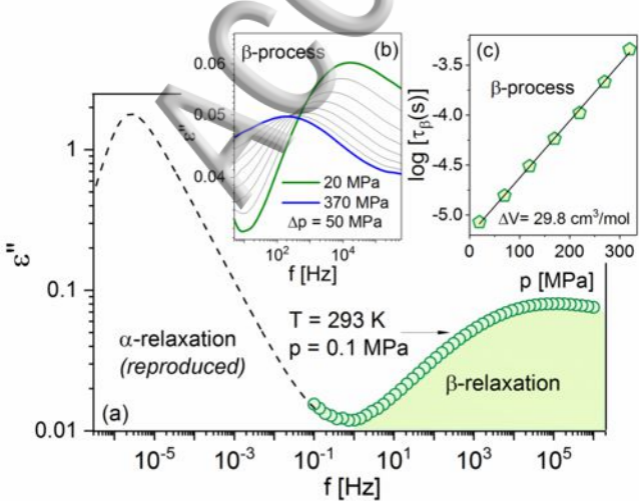
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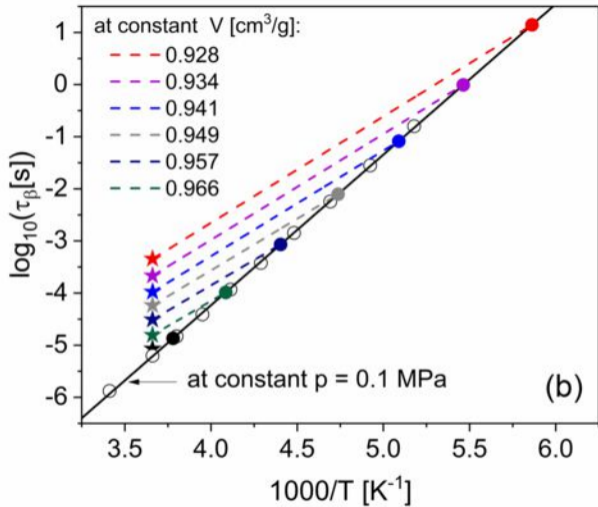
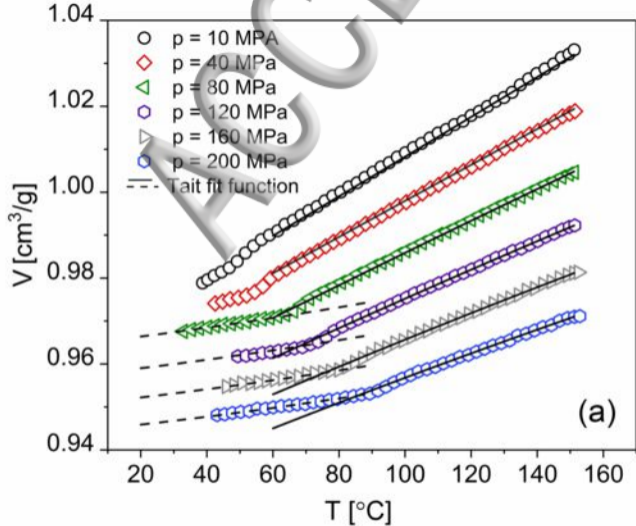
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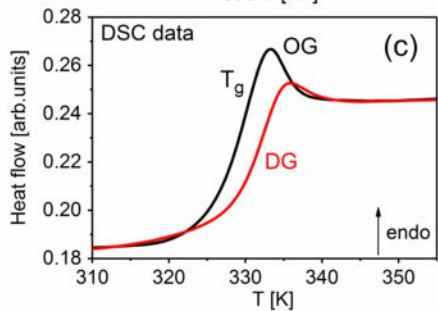
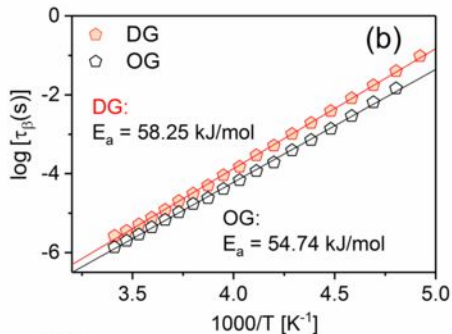
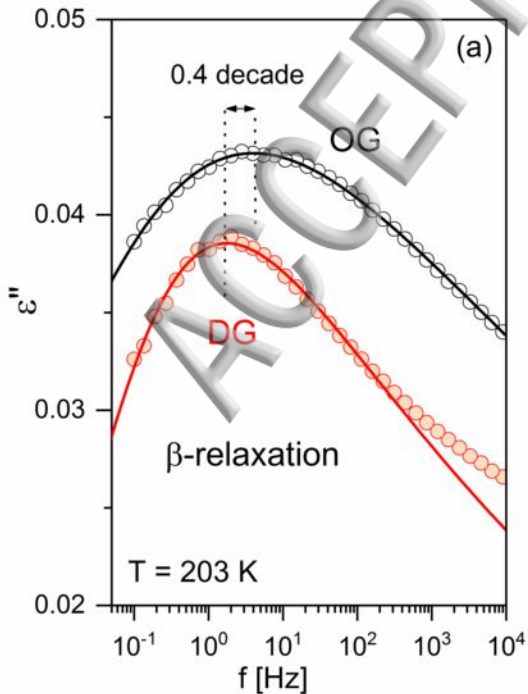
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Structure factor $S(Q)$

2
1
0

0

Scattering vector Q [\AA^{-1}]

4

8

12

16

■ OG

● DG

— 1 molecule

23
22
21

1.2

1.3

1.4

1.5

1.6

