



HAL
open science

Is the Johari-Goldstein β -relaxation universal?

Mohamed Shahin Thayyil, Simone Capaccioli, Daniele Prevosto, Kia Ling Ngai

► **To cite this version:**

Mohamed Shahin Thayyil, Simone Capaccioli, Daniele Prevosto, Kia Ling Ngai. Is the Johari-Goldstein β -relaxation universal?. *Philosophical Magazine*, 2008, 88 (33-35), pp.4007-4013. 10.1080/14786430802270082 . hal-00513923

HAL Id: hal-00513923

<https://hal.science/hal-00513923>

Submitted on 1 Sep 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Is the Johari-Goldstein β -relaxation universal?

Journal:	<i>Philosophical Magazine & Philosophical Magazine Letters</i>
Manuscript ID:	TPHM-08-May-0165
Journal Selection:	Philosophical Magazine
Date Submitted by the Author:	15-May-2008
Complete List of Authors:	Thayyil, Mohamed Shahin; University of Pisa, Dipartimento di Fisica Capaccioli, Simone; CRS SOFT - CNR INFM, Physics Prevosto, Daniele; Department of Physics Ngai, Kia; Naval Research Laboratory, Code 6807
Keywords:	amorphous materials, glass transition
Keywords (user supplied):	dielectric relaxation, glassforming liquids, secondary relaxation



Catchline (head of first page only) *Philosophical Magazine*, Vol. X, No. X, Month 2008, xxx–xxx, special issue

Running heads (verso) *M. Shahin Thayyil et al.*
(recto) *Is the Johari-Goldstein relaxation universal?*

Article Type (Research paper)

Is the Johari-Goldstein β -relaxation universal?

MOHAMED SHAHIN THAYYIL*†‡, SIMONE CAPACCIOLI†, DANIELE PREVOSTO† and KIA L. NGAI§

† CNR-INFM, polyLab, & Physics Department, Università degli Studi di Pisa, Largo Pontecorvo 3, I-56127 Pisa (Italy)

‡ Department of Physics, University of Calicut, Kerala, INDIA

§ Naval Research Laboratory, Washington DC 20375-5320 USA

Correspondence *Corresponding author. Email: shahin@df.unipi.it

Abstract

The Johari-Goldstein (JG) β -relaxation is supposedly a universal feature in glassy dynamics and has strong connections to the structural α -relaxation in all glassformers. However, against the hypothesis of its universality are some greatly studied small molecular glassformers which give no indication that JG relaxation is present despite investigations using a variety of experimental techniques. These exceptions cast doubt on its universal nature and fundamental importance. Theoretical consideration suggests that the JG β -relaxation is present but not resolved in these glassformers because it is sandwiched between the more intense α - and a faster but non-JG secondary γ -relaxation. We investigate such suggestion on several glass formers and we report herein representative data on benzophenone and dimethyl phthalate. We show that by dissolving any of these glassformers in hosts with much higher glass transition temperatures, we were able to move the α -relaxation further away from the γ -relaxation, and find the JG β -relaxation for the first time in two glassformers of current interest in the research community.

Keywords: dielectric relaxation; glassforming liquids; secondary relaxation; benzophenone; dimethylphthalate

PACS Subject Classification: 77.22.-d; 77.22.Gm; 61.20.Lc; 83.85.Ns; 83.50.Xa

1 Introduction

Recent empirical investigations [1], experiments [2--9], and simulations [10] have shown there exists a class of secondary relaxations with properties that either mimic or are correlated with the primary structural α -relaxation of glassforming substances. This connection with the α -relaxation suggests that the secondary relaxations within this class are fundamental and play a role in the dynamics leading to the α -relaxation. In order to distinguish this important class of secondary relaxations from others, it was proposed to call them Johari-Goldstein (JG) β -relaxations [11]. This nomenclature serves also to honour the important discovery by JG that totally rigid glassformers have secondary relaxation. If the JG β -relaxation is truly of fundamental importance, a prerequisite is its presence in all glassformers. Although this requirement is fulfilled in many common as well as in some exotic glassformers such as plastic crystals [12], inorganic oxide glasses [13], the molten salt $0.4\text{Ca}(\text{NO}_3)_2\text{-}0.6\text{KNO}_3$ (CKN) [14], and metallic glasses [15--19], there are cases where normal experimental procedure has not been able to produce evidence of the existence of the JG β -relaxation. Ironically, these cases are found in small molecular and organic glassformers, a class of materials that have usually shown the presence of the JG β -relaxation by dielectric relaxation spectroscopy [20]. This conundrum raises serious question on the proposal that the JG β -relaxation plays an important role in glass transition. In some of these cases, application of special procedure such as aging the glassformer in the glassy state [21--24] or elevating the pressure [25--28] were able to find the JG β -relaxation by resolving it from the higher intensity α -relaxation appearing at lower frequencies, and sometimes also from the high frequency non-JG secondary relaxation. However, there are some glassformers for which none of these procedures have produced evidence for the presence of the JG β -relaxation. These glassformers include the lower members of the dialkyl phthalates, viz. dimethyl phthalate (DMP), diethyl phthalate (DEP) [29], and dibutyl phthalate (DBP) [30] or diisobutyl phthalate (DiBP). A secondary γ -relaxation is present in all these phthalates, but it is not the JG β -relaxation we are looking for because its dynamics bear no correlation with the α -relaxation. For example, its relaxation time is insensitive to applied pressure, in stark contrast to the α -relaxation time, τ_α [29]. Based on the chemical structure of the phthalates, this γ -relaxation is related to rotation of the alkyl group about the flexible oxygen bond and only involves a part of the molecule. These phthalates are good glassformers and extensively used in industry for various purposes. Their dynamic properties over broad frequency/time range have been studied by several experimental techniques including optical Kerr effect [31], dynamic light scattering [32], dielectric relaxation measurements at ambient and elevated pressures [30, 33, 34], and inelastic X ray scattering [35]. The results of these studies have impact on theoretical models of glass transition [36--38]. Another glassformer with similar situation as the phthalates is benzophenone (BZP) [31, 39, 40]. In fact, although BZP shows a well resolved secondary relaxation, there is some evidence that such process could be of intramolecular nature [41, 42]. The lack of evidence of the presence of JG β -relaxation in some well studied glassformers including the phthalates and BZP can undermine its importance in glass transition. In a log-log plot of dielectric loss against frequency, the high frequency flank of the α -loss peak of the phthalates and BZP have maximum absolute value of the slope near 0.5. If the JG β -relaxation of the phthalates and BZP indeed were non-existent, then these exceptional cases may even invite the interpretation of α -relaxation which gives little importance to the JG β -relaxation [43, 44].

Whenever the JG β -relaxation is resolved, its relaxation time τ_{JG} is approximately the same as the primitive relaxation time τ_0 of the Coupling Model (CM) [1], which can be calculated from τ_α and the stretch exponent of the Kohlrausch correlation function of the α -relaxation. It turns out the calculated τ_0 , and hence the expected τ_{JG} , of the phthalates (see Fig.4 in [30]) and BZP is located in between the α - and the γ -relaxations. Thus, it is possible that the JG β -relaxation cannot be resolved in these glassformers because it is sandwiched between the slower and much more intense α -relaxation on one side and the faster non-JG γ -relaxation on the

other side. To resolve the JG β -relaxation we must increase the separation between the α - and the γ -relaxations. One way to do this is by mixing the phthalates and BZP with a host that have a much higher glass transition temperature T_g . The presence of the less mobile host molecules slows down the α -relaxation of the phthalate molecules in the mixture more than in the neat phthalate. On the other hand, the local and intramolecular γ -relaxation is not as sensitive to the presence of the host molecules. Hence, the increased separation between τ_α and τ_γ of the phthalate in the mixture gives a better chance for the supposedly universal JG β -relaxation to be resolved. This method is effective for dielectric spectroscopy when the host molecules is apolar like oligomers of styrene or ortho-terphenyl (OTP), and the dynamics of the polar phthalates or BZP are seen exclusively in the observed dielectric spectra. The objective of this paper is to apply this method to the phthalates and BZP by mixing with low molecular weight polystyrene, and demonstrate that the JG β -relaxation exist in DMP, DEP, DBP, DiBP, and BZP. Due to space limitation, only isochronal data of DMP and BZP are reported here, as representative of all the materials. Broadband isothermal dielectric relaxation data taken at various temperatures of all these glassformers in the pure state as well as in mixtures will be reported elsewhere.

2 Experimental Section

Dimethylphthalate (DMP, $T_g = 193$ K), benzophenone (BZP, $T_g = 207$ K), and *o*-terphenyl (OTP, $T_g = 244$ K), were obtained from Aldrich and used as received. Polystyrene 800 (PS800) with molecular weight=820 g mol⁻¹, $M_w/M_n=1.01$, and $T_g=282$ K was obtained from Scientific Polymer Products. All samples were stored and handled in dry nitrogen atmosphere. The polar molecules were dissolved in PS800 and OTP at molar concentration of about 10% (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

In order to show the method we used to find the JG β -relaxation in the phthalates and BZP works and is general, we present the results in a previous study of a lesser known dipolar glassformer, butylacetate (BuAc, $T_g = 125.7$ K) [45]. Figure 1 shows the temperature dependence of isochronal (i.e. obtained at 1 kHz) dielectric loss ϵ'' data of neat BuAc, 10 wt% BuAc in isopropylbenzene (IPB, $T_g=128.5$ K), and 10 wt% BuAc in *o*-terphenyl (OTP, $T_g = 244$ K). Shown in the same figure is the chemical structure of BuAc together with the rotation of the -OOC-CH₃ group around its oxygen bond. This internal motion is responsible for the γ -relaxation of neat BuAc seen as a maximum of ϵ'' at $T=109$ K (Fig. 1). The T_g of IPB is only 3 degrees higher than that of BuAc, and the mixing shifts the isochronal α -loss peak (at 1 kHz) from about 139.5 K of neat BuAc to 149 K of BuAc in IPB. The shift of less than 10 degrees is too small to significantly increase the separation between τ_α and τ_γ of the BuAc in this mixture to resolve the JG β -relaxation. A much higher T_g of the host, like OTP, is required towards this goal. In fact, isochronal loss spectra at 1 kHz of BuAc in OTP (Fig.1) show that the α -loss peak has been shifted from about 139.5 K for neat BuAc to 245 K for BuAc in OTP. On the other hand, the shift of the γ -loss peak is small as expected for local and intramolecular secondary relaxation. It is clear by inspection of Fig.1 that a new secondary relaxation appears in the isochronal spectrum of BuAc in OTP concomitant with the large separation between τ_α and τ_γ of the BuAc in OTP.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Our mixture of 0.095 mole fraction of DMP in PS800 satisfies the requirement of large difference in T_g of the dipolar guest DMP ($T_g=193$ K) in the apolar host PS800 ($T_g=282$ K) for resolving the so far unseen JG β -relaxation of DMP. The isochronal dielectric loss data at 1 Hz of DMP in neat DMP and in 0.095 molar fraction of DMP in PS800 are presented in Fig.2. The large shift to high temperatures of the α -loss peak of DMP when dissolved in PS800 is evident. There is only a small shift of the γ -loss peak, as it is expected, since its origin involves an intramolecular mechanism (i.e. rotation of the alkyl group about the oxygen bond), and the different environment for the molecule due to the mixing cannot perturb too much the energy barrier for the internal motion. These drastically different behaviours of the α - and γ -relaxations are found also in the isothermal spectra (not shown). A new secondary relaxation appears at temperatures intermediate between the α - and the γ -loss peaks. This new secondary relaxation is the JG β -relaxation of DMP that we are looking for. It is the JG β -relaxation because it is the slowest secondary relaxation, and hence conceivably involves the motion essentially the entire DMP molecule.

BZP shows the same change of the isochronal dielectric spectrum when it is dissolved in PS800 at 0.123 mole fraction. As shown in Fig.3, the shift of the isochronal α -loss peak of BZP at 1 Hz by about 50 K is substantial, and again the position of the γ -loss peak remains unchanged. In the glassy state a very broad process is then present, envisaging the presence of an additional process. The new secondary relaxation located at temperatures intermediate between the α - and the γ -loss peaks is the JG β -relaxation of BZP. Isothermal spectra of neat BZP and 0.123 mole fraction of BZP in PS800 (not shown) are consistent with the isochronal data. The relaxation times τ_γ of BZP in the mixture of 0.123 mole fraction of BZP in PS800 are within experimental errors the same as that determined by P. Lunkenheimer and co-workers [46] and by S. Walker and co-workers [47]. The new secondary relaxation that we identify as the JG β -relaxation of BZP was not found in the broadband dielectric spectra of neat BZP at temperatures above and below glass transition [40, 46].

4 Conclusion

The dialkylphthalates, including the dimethyl, diethyl, dibutyl, and diisobutyl phthalates, as well as benzophenone are important in the research of glass transition because they have been extensively studied by several different techniques over immense time/frequency range, and the results have made broad impact on various theoretical understanding. Despite these previous experimental studies, there is no evidence of the presence of the supposedly universal Johari-Goldstein (JG) β -relaxation in these glassformers. On the contrary, an intramolecular secondary relaxation process dominates the glassy dynamics in the absence of the intermolecular JG β -relaxation. Its apparent absence in these important glassformers could create serious doubt on the universal and fundamental nature of the Johari-Goldstein β -relaxation. Possible cause of this situation is a combination of two factors: the JG β -relaxation is not sufficiently separated from the dominant α -relaxation and it is sandwiched between the α -relaxation and the resolved non-JG γ -relaxation. Theoretical consideration suggests these impediments can be alleviated by probing the dynamics of these glassformers in mixtures with another glassformer having significantly higher T_g . Experimental data reported here confirms the presence of the JG β -relaxation in benzophenone and dimethyl phthalate. Moreover, the same result was found in other phthalates.

Acknowledgements

The work at the Università di Pisa was supported by MIUR-FIRB 2003 D.D.2186 grant RBNE03R78E. MST kindly acknowledges the support from MIUR (“Borse a favore di giovani ricercatori indiani”, n. 1451,

28/07/2005"). KLN was supported by the Office of Naval Research and a grant for International Semester Exchange Collaboration provided by International Materials Institute for New Functionality in Glass.

References

- [1] K. L. Ngai, *J. Chem. Phys.* **109**, 6982 (1998).
- [2] G. P. Johari and M. Goldstein, *J. Chem. Phys.* **53** 2372 (1970). G. P. Johari, *J. Non-Cryst. Solids* **307–310** 317 (2002).
- [3] E. Kaminska, K. Kaminski, and M. Paluch, K. L. Ngai, *J. Chem. Phys.* **124**, 164511 (2006).
- [4] M. Mierzwa, S. Pawlus, M. Paluch, E. Kaminska, K. L. Ngai, *J. Chem. Phys.* **128**, 044512 (2008).
- [5] K. Kessairi, S. Capaccioli, D. Prevosto, M. Lucchesi, S. Sharifi, P.A. Rolla, *J. Phys. Chem. B* **112**, 4470 (2008).
- [6] A. Nogales, A. Sanz, T. A. Ezquerra, *J. Non-Cryst. Solids*, **352**, 4649 (2006).
- [7] D. Prevosto, S. Capaccioli, S. Sharifi, K. Kessairi, M. Lucchesi, P. A. Rolla, *J. Non-Cryst. Solids*, **353**, 4278 (2007).
- [8] R. Böhmer, G. Diezemann, B. Geil, G. Hinze, A. Nowaczyk, M. Winterlich, *Phys. Rev. Lett.* **97**, 135701 (2006).
- [9] A. Nowaczyk, B. Geil, G. Hinze, R. Böhmer, *Phys. Rev. E* **74**, 041505 (2006).
- [10] D. Bedrov and G. D. Smith, *Macromolecules* **38**, 10314 (2005), *ibid.* **39**, 8526 (2006).
- [11] K. L. Ngai and M. Paluch, *J. Chem. Phys.* **120**, 857 (2004).
- [12] R. Brand, P. Lunkenheimer, A. Loidl, *J. Chem. Phys.* **116**, 10386 (2002).
- [13] J. M. Pelletier, J. Perez, L. Duffrene, A. Sekkat, *J. Non-Cryst. Solids*, **258**, 119 (1999).
- [14] C. Mai, S. Etienne, J. Perez, and G. P. Johari, *Philos. Mag. B* **50**, 657 (1985)
- [15] J. M. Pelletier, B. Van de Moortele, I. R. Lu, *Mater. Sci. Eng. A* **336**, 190 (2002).
- [16] P. Rösner, K. Samwer, P. Lunkenheimer, *Euro. Phys. Lett.* **68**, 226 (2004).
- [17] K. L. Ngai, *J. Non-Cryst. Solids*, **352**, 404 (2006).
- [18] P. Wen, D. Q. Zhao, M. X. Pan, W. H. Wang, Y. P. Huang, and M. L. Guo, *Appl. Phys. Lett.* **84**, 2790 (2004).
- [19] J. Hachenberg, D. Bedorf, K. Samwer, R. Richert, A. Kahl, M. D. Demetriou and W. L. Johnson, *Appl. Phys. Lett.* **92**, 131911 (2008).
- [20] A. Kudlik, S. Benkhof, T. Blochowicz, C. Tschirwitz, E. Rössler, *J. Mol. Struct.* **479**, 201 (1999).
- [21] U. Schneider, R. Brand, P. Lunkenheimer, and A. Loidl, *Phys. Rev. Lett.* **84**, 5560 (2000).
- [22] K. L. Ngai, P. Lunkenheimer, C. León, U. Schneider, R. Brand, and A. Loidl, *J. Chem. Phys.* **115**, 1405 (2001)
- [23] E. Kaminska, K. Kaminski, S. Hensel-Bielowka, M. Paluch and K. L. Ngai, *J. Non-Cryst. Solids*, **352**, 4672 (2006).
- [24] D. Prevosto, S. Capaccioli, M. Lucchesi, P. A. Rolla and K. L. Ngai, *J. Chem. Phys.* **120** 4808 (2004).
- [25] R. Casalini and C. M. Roland, *Phys. Rev. Lett.* **91**, 015702 (2003).
- [26] S. Capaccioli, D. Prevosto, M. Lucchesi, P. A. Rolla, R. Casalini and K. L. Ngai, *J. Non-Cryst. Solids* **351** 2643 (2005).
- [27] S. Hensel-Bielowka, M. Paluch and K. L. Ngai, *J. Chem. Phys.* **123**, 014502 (2005).
- [28] K. Kaminski, E. Kaminska, M. Paluch, J. Ziolo, and K. L. Ngai, *J. Phys. Chem. B* **110**, 25045 (2006).
- [29] S. Pawlus, M. Paluch, M. Sekula, K. L. Ngai, S. J. Rzoska, and J. Ziolo, *Phys. Rev. E* **68**, 021503 (2003).
- [30] M. Sekula, S. Pawlus, S. Hensel-Bielowka, J. Ziolo, M. Paluch and C. M. Roland, *J. Phys. Chem. B* **108**, 4997 (2004).

- 1
2
3 [31] H. Cang, V. N. Novikov, M.D. Fayer, J. Chem. Phys. **118**, 2800 (2003).
4 [32] A. Brodin, R. Bergman, J. Mattsson and E.A. Rössler, Eur. Phys. J. B **36**, 349–357 (2003).
5 [33] S. K. Nayak and S. S. N. Murthy, J. Chem. Phys. **99**, 1607 (1993).
6 [34] K. Niss, C. Dalle-Ferrier, G. Tarjus and C. Alba-Simionesco, J. Phys.: Condens. Matter **19**, 076102
7 (2007).
8 [35] A. Mermet, E. Duval, A. Polian, and M. Krisch, Phys. Rev. E **66**, 31510 (2002).
9 [36] W. Götze, M. Sperl, Phys. Rev. Lett. **92**, 105701 (2004).
10 [37] M. Sperl, Phys. Rev. E **74**, 011503 (2006).
11 [38] H. Z. Cummins, J. Phys.: Condens. Matter **17**, 1457 (2005).
12 [39] A. Brodin, C. Gainaru, V. Porokhonsky, E. A. Rössler, J. Phys.: Condens. Matter, **19**, 205104 (2007).
13 [40] L. C. Pardo, P. Lunkenheimer, A. Loidl, Phys. Rev. E **76**, 030502(R) (2007).
14 [41] K. M. Gough and T. A. Wildman, J. Am. Chem. Soc. **112**, 9141 (1990).
15 [42] Z. Rappoport, S. E. Biali and M. Kaftory, J. Am. Chem. Soc. **112**, 7742 (1990).
16 [43] N. B. Olsen, T. Christensen, J. C. Dyre, Phys. Rev. Lett. **86**, 1271 (2001).
17 [44] A. I. Nielsen, T. Christensen, B. Jacobsen, K. Niss, B. Olsen, R. Richert, and J.C. Dyre,
18 arXiv:0712.2827v
19 [45] Md. Shahin and S. S. N. Murthy, J. Chem. Phys. **122**, 014507 (2005).
20 [46] P. Lunkenheimer, L. C. Pardo, M. Köhler and A. Loidl, Phys. Rev. E **77**, 031506 (2008).
21 [47] M. A. Desando, D. L. Gourelay and S. Walker, J. Chem. Soc. Faraday Trans. 2 **79**, 559 (1983).
22
23
24
25
26
27
28

Figure Captions

29
30
31 Figure 1. Logarithm of dielectric losses at 1 kHz versus temperature for butylacetate: pure (triangles), mixed with IPB (stars), mixed
32 with OTP (open circles). Lines are guides for eyes. Inset shows the molecular structure and the internal rotation related to the γ
33 relaxation.
34

35 Figure 2. Logarithm of dielectric losses at 1 Hz versus temperature for DMP: pure (open circles) and mixed with PS800 (full circles)
36 Lines are guides for eyes.
37

38 Figure 3. Logarithm of dielectric losses at 1.35 Hz versus temperature for BZP: pure (open circles) and mixed with PS800 (full
39 circles) Lines are guides for eyes.
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Figures

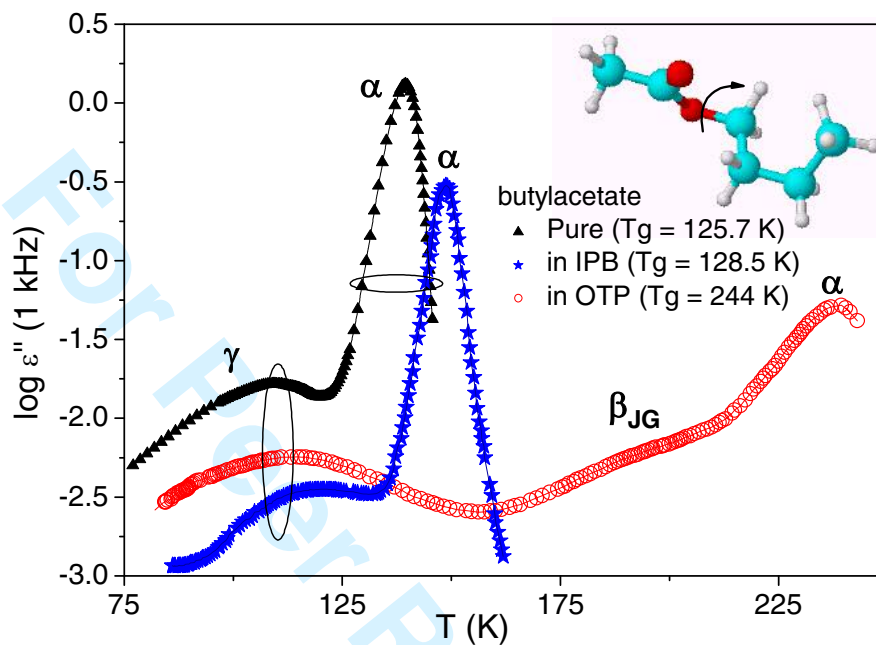


Figure 1

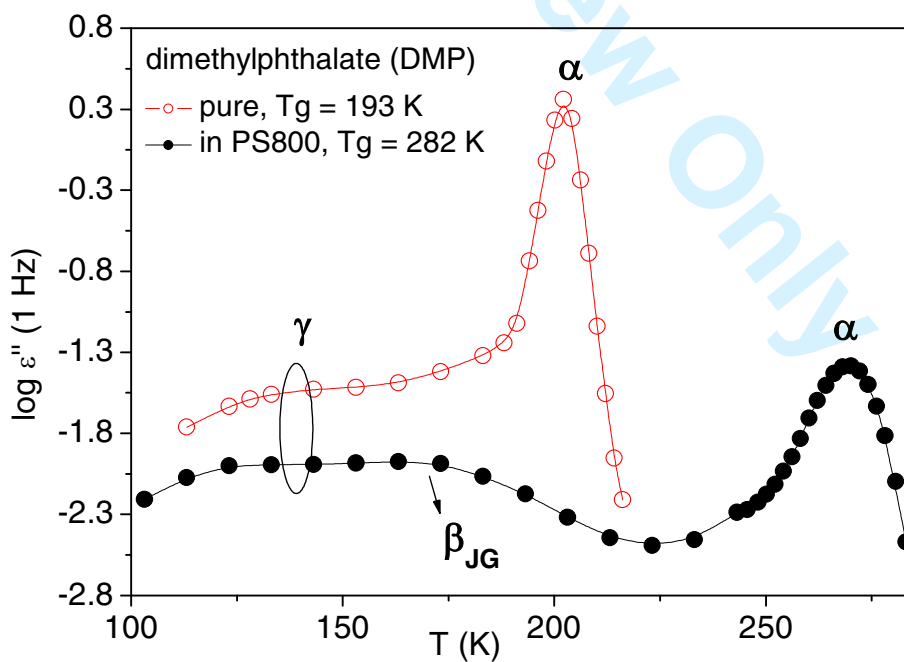


Figure 2

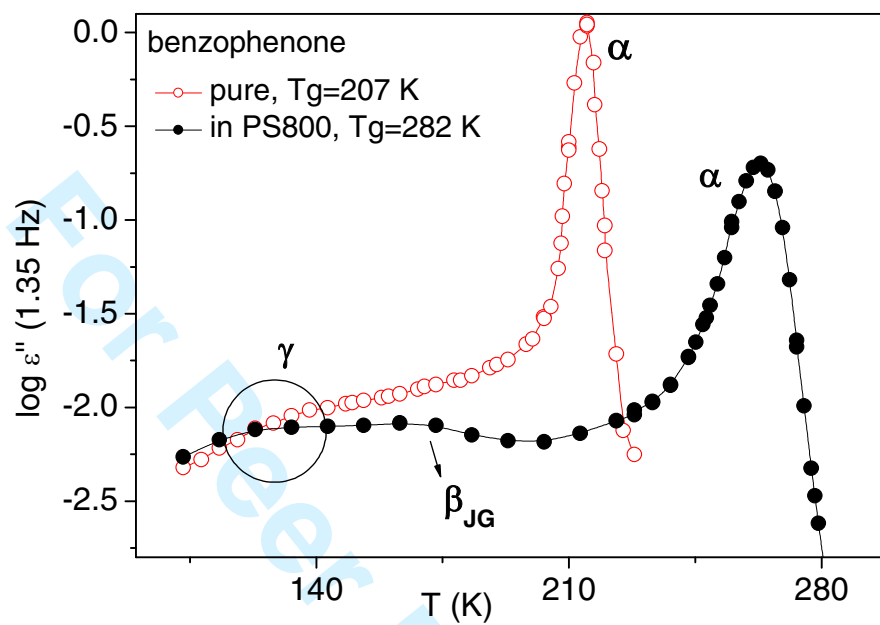


Figure 3